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Homologous series of n-alkanes (C_{19} - C_{35}), fatty acids (C_{12} - C_{32}) and nalcohols (C_8 - C_{30}) in atmospheric aerosols from central Alaska: Molecular distributions, seasonality and source indices



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ABSTRACT

To better understand the molecular distributions, seasonality and source indices of organic aerosols in central Alaska, we measured homologous series of n-alkanes (C19-C35), fatty acids (C12-C32) and n-alcohols (C8-C30) in total suspended aerosols collected during June 2008 to 2009 using a gas chromatography/mass spectrometry (GC-MS). The whole sampling period was divided as warm (early May to late September; summer) and cold (late September to early May; winter) periods. Molecular distribution was characterized in both periods by the predominance of C25 for n-alkanes and C24:0 for fatty acids. However, we noticed a difference in molecular distribution of n-alcohols between warm and cold periods, which was characterized by the predominance of C_{22} in warm season while C26 in cold period. Except for fatty acids, n-alkanes and n-alcohols showed higher concentrations in warm period than in cold period. We found significantly higher ratios of $C_{18:1}/C_{18:0}$ in warm period than those in cold period, suggesting the fresh biogenic and aged anthropogenic aerosols in warm and cold periods, respectively. This inference was consistent with significantly higher ratios of WSOC/OC, a proxy for photochemical aging, in cold period. Based on the carbon preference index (CPI), average chain length (ACL), low-to-high molecular weight (LMW/HMW) ratios, wax n-alkanes (%WNA) and estimated fossil fuel concentrations, we demonstrate that higher plant waxes, biomass burning from wildfires are two important sources in warm period while combustion derived anthropogenic emissions are major sources in cold period in central Alaska. This finding was further supported by higher ratios of nss-K⁺/elemental carbon (EC) and methanesulfonate (MSA⁻)/EC ratios in warm period.

1. Introduction

Lipids or aliphatic hydrocarbons are ubiquitous and important class of organic compounds in the atmosphere (Fu et al., 2008; Kawamura et al., 2003; Ren et al., 2016). Due to their chemical stability and longlifetime, these compounds have been used as source signatures to ascertain the origin and type of organic aerosols (OA) (Gagosian et al., 1981; Simoneit et al., 1991). For instant, n-alkanes majorly originate from both anthropogenic and biogenic sources including petroleum residues, diesel engine (Simoneit, 1984) and biomass burning (Simoneit, 2002; Simoneit and Elias, 2000, 2001) as well as terrestrial plant wax, fungi, bacteria, algae and plankton (Brown et al., 2002). Further, plant wax n-alkanes are used directly as a proxy for both atmospheric transport and origin of OA in the atmosphere (Fang et al., 1999; Lyu et al., 2017; Tang et al., 2006). Thus, the present study on lipids class organic compounds in atmospheric aerosols is a noteworthy attempt.

Fatty acids (FAs) are the most abundant components among all lipids and unsaturated FAs are important precursors for secondary organic aerosols (SOA) as pioneered by Kawamura and Gagosian (1987). Literature studies have suggested that fatty acids are emit directly from surface of plant leaves (Rogge et al., 1993), wood combustion (Fine

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et al., 2001), biomass burning (Simoneit, 2002), meet cooking (Schauer et al., 1999) and marine biota (Kawamura and Gagosian, 1987). n-Alcohols are one of the important and typical biomarker compounds that mainly originate from epicuticular plant waxes of terrestrial higher plants (Fu et al., 2008; Wang and Kawamura, 2005). Thus, studying source-specific lipid components in the ambient aerosols are important and provide more detailed insights into a perceptive estimation of various anthropogenic and biogenic impacts on the environment and public health as well.

Carbon preference index (CPI) is one of the important source indices to describe the molecular distribution of longer chain ($C \ge 20$) lipids (Marzi et al., 1993; Pietrogrande et al., 2010). CPI values reflect the differences of the relative concentrations between odd-carbon- and even-carbon-numbered long-chain hydrocarbons in a certain carbon number range. The carbon maximum number, C_{max}, has been widely used to signify the source strengths of anthropogenic verses biogenic emissions. Likewise, average chain length (ACL), low-to-high molecular weight (LMW/HMW), plant wax n-alkane percent (WNA%), etc., have been widely used to infer the relative contributions from various sources to lipids in different environmental conditions (Lyu et al., 2017; Ren et al., 2016; Tanski et al., 2017). Further, the relative abundances of n-alkanes, fatty acids and n-alcohols of longer chain (high molecular weight) are used to differentiate the source regions of terrestrial biomarkers (Bendle et al., 2006; Kang et al., 2016; Kawamura et al., 2003; Ren et al., 2016).

Alaska is the largest state in the United States and geographically existed in a subarctic region (Fig. 1). It spans a wide range of climatic and ecological conditions that include rainforests, glaciers, boreal forest, tundra, peat lands, and meadows. Thus, biogenic emissions from these ecosystems are considered to make a significant contribution to secondary OA in subarctic Alaska (Haque et al., 2016). To better understand the characteristics and sources of OA and their seasonal variations in Alaska, we conducted one year observation of total suspended particulate matter (TSP) collected from Fairbanks, central Alaska. Fairbanks is a largest city in the interior of Alaska, located in the Tanana valley, surrounded by mountains on three sides (see enlarged picture in Fig. 1), contributes to temperature inversions that often occur throughout winter (Ward et al., 2012). Fairbanks in central Alaska has some of the highest measured ambient aerosol concentrations in the United States, with wintertime levels often exceeding the National Ambient Air Quality Standard (NAAQS) (Ward et al., 2012). The National Emission Inventory database from 2008 shows that the major sources of air pollution at Fairbanks are fuel combustion (coal and oil), diesel emissions, vehicle exhaust (snow machines, all-terrain vehicles (ATVs) etc.), wildfires, waste disposal, aircraft emissions, petroleum refineries, road dust and wood combustion (Shakya and Peltier, 2013; Ware et al., 2013). Fuel oil and wood stoves are most commonly used for room heating in Alaska during winter in addition to open biomass burning (Ware et al., 2013). Therefore, it is important to understand the sources of aerosols in an air shed of Fairbanks.

In this study, we address the molecular distributions of homologous series of n-alkanes (C_{19} - C_{35}), fatty acids (C_{12} - C_{32}) and n-alcohols (C_8 - C_{30}) and their seasonality in total suspended particulate (TSP) aerosols collected during June 2008–June 2009 in Alaska. We discuss the possible sources of lipids in two distinct climatic periods in Alaska. To the best of our knowledge, this is the first time to determine the homologous of aliphatic hydrocarbons in ambient aerosols over Alaska.

2. Methodology

2.1. Aerosol sampling

TSP samples (n = 32) were collected on pre-combusted (450 °C for 6 h) quartz fibre filters (47 mm, HEPA, Pall Corporation, USA) from June 2008 to June 2009 using a low-volume air sampler (NIER) with a flow rate of $16.7 \text{ L} \text{ min}^{-1}$ at University of Alaska (64.85° N; 147.85° W),

Fairbanks, Alaska. Fig. 1 shows the location of sampling site and its adjacent regions. The air sampler was set up on the rooftop of the International Arctic Research Centre (IARC) building at university campus. Aerosol sampling was performed roughly on every one to three weeks during the study period. After sampling, filters were kept in a pre-combusted (450 °C for 6 h) glass vial (50 ml) with a Teflon lined screw cap and stored at -20 °C until the analysis of lipid class compounds. Field blank samples (n = 6) were collected by placing in the cartridge of air sampler for 10 to 15 Sec without running the pump.

2.2. Meteorological parameters

Fig. 2 presents the temporal variation of daily mean meteorological parameters including temperature, barometric pressure, wind speed and wind direction at the sampling site during June 2008 to June 2009. All the meteorological parameters were downloaded from the weather underground company, USA (https://www.wunderground.com/). Based on the variations of meteorological data and subarctic climate over Alaska, we divided the whole sampling period as warm (early May to late September; summer) and cold (late September to early May; long winter) periods. Daily average temperatures ranged from 0 °C to 21 °C (mean: 12 ± 5 °C) in warm period while those ranged from -43 °C to -1 °C (-17 ± 9 °C) in cold period (Fig. 2a). In contrast, daily mean relative humidity ranged from 21% to 93% (58 \pm 12%) and 52% to 100% (87 \pm 12%) during warm and cold periods, respectively. High speed and low pressure westerly winds are dominated during warm period, whereas low speed and high pressure easterly winds are more common in cold period (Fig. 2b-d). Total precipitations were 197 mm and 30 mm during warm and cold periods, respectively. Based on the 7day backward air mass trajectory analysis, Haque et al. (2016) reported that there are no significant changes in the air mass patterns between cold and warm periods, hence local sources/meteorology are important during the sampling period in the Alaska.

2.3. Determination of lipid class components

We analyzed the aerosol samples for lipid class components (n-alkanes, fatty acids, and n-alcohols) using the analytical method described elsewhere (Fu et al., 2008). Briefly, an aliquot (Ø 20 mm) from each filter sample was extracted with 7 mL of dichloromethane (DCM) and methanol (MeOH) mixture (2:1 v/v) under ultrasonication $(10 \min \times 3 \text{ times})$ at room temperature. The solvent extracts were filtrated through a Pasteur pipette packed with quartz wool to remove the filter debris. After filtrating, the supernatants were concentrated using a rotary evaporator under vacuum and then blown down to dryness using pure N2 (nitrogen) gas. The dried extracts were then reacted with 50 µL of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10 µL of pyridine at 70 °C for 3 h to make COOH and OH groups derivatized to TMS (trimethylsilyl) easters and ethers, respectively, and then finally, the solutions (derivatives) were diluted with 40 µL of n-hexane (which containing an internal standard, C13 n-alkane, 1.43 ng/µL) and then immediately analyzed using gas chromatography/mass spectrometry (GC/MS).

GC (Hewlett-Packard 6890) coupled with a mass-selective detector (MSD; Hewlett-Packard 5973) was used to measure the lipid class components in aerosol samples. More detailed information of GC-MS instrumentation was available in supporting information (SI). GC/MS mass spectral data were acquired and processed using the Chemstation software. Individual compounds of trimethylsilyl derivatives were identified by comparison of mass spectra with those of authentic standards and literature data (Fu et al., 2008). The quantification of organic compounds and their analytical errors were described in elsewhere (Haque et al., 2016). Recoveries of the authentic standards of lipids that were spiked on the pre-combusted blank filters were generally better than 80%. We also have analyzed filed blank samples (n = 4) and target compounds were not detected in the field blanks. Relative standard





Fig. 1. Location of the sampling site, Fairbanks (64°51′ N; 147°51′ W), Alaska. The enlarged map showing the sampling locality in Fairbanks city surrounded by hills on three sides.

deviations for the target compounds in replicate analyses were less than 10%.

2.4. EC, OC, WSOC and major ion analyses

To better support the inferences related to lipid class components in central Alaska, we used chemical composition data, including elemental carbon (EC), organic carbon (OC), water-soluble organic carbon (WSOC) and water-soluble ionic tracers (methanesulfonate, MSA⁻ and non sea salt potassium, nss-K⁺). EC and OC were determined using a Sunset Lab Carbon Analyzer, following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evaluation protocol (Boreddy et al., 2018). WSOC and ionic species were determined using TOC analyzer and an ion chromatograph (Compact IC 761; Metrohm, Switzerland), respectively (Boreddy et al., 2018; Boreddy and Kawamura, 2015). More detailed information about the analytical procedures and uncertainties of chemical species were available in SI. All the chemical composition data reported in this study were corrected for field blanks.

2.5. Mann-Whitney U test

Mann-Whitney *U* test is the non-parametric test, which compares two groups without making the assumption that values are normally distributed (Bergmann et al., 2000) and is often used in aerosol studies to detect the significant levels in two groups (Kang et al., 2016). In this study, we used XLSTAT software (https://www.xlstat.com/en/) to perform the Mann-Whitney *U* test analysis.

3. Results and discussion

3.1. Molecular distributions

Fig. 3(a–c) presents the mean molecular distributions of homologous series of n-alkanes, fatty acids and n-alcohols for warm and cold periods in central Alaska during June 2008 to June 2009. The mean concentrations of all lipid components were significantly higher in warm period than those in cold period.

It has been suggested that C_{23} and C_{25} are the signatures for anthropogenic activities (for example, petroleum residues) whereas C_{27}



Fig. 2. Daly mean variations of meteorological parameters (a) temperature and dew point, (b) barometric pressure, (c) wind speed, and (d) wind direction during June 2008 to June 2009 at the Alaska, downloaded from the web site https://www.wunderground.com/. Warm (early May to late September) and cold (late September to early May) periods are indicated by light blue and pink colors, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

mainly comes from the higher plant waxes (Simoneit et al., 1991). Further, Kawamura et al. (2003) reported that predominance of C₂₉ and C31 in terrestrial higher plants and emergent/aquatic plants. These biomarkers also arise from natural sources (plant litter from garden soil, road dust) and biomass burning which redistributes plant waxes in the atmosphere (Rogge et al., 1993; Yadav et al., 2013). In this view, molecular distributions of n-alkanes in central Alaska were characterized by a strong odd-carbon numbered predominance with maxima (Cmax) at C25 followed by C27 and C23 for both the periods. This result suggests that n-alkanes in central Alaska were likely dominated by anthropogenic as well as biogenic emissions. The predominance of low carbon number (C19-C25) of n-alkanes in cold period indicates a dominance of anthropogenic sources. We found significant concentrations of C29 and C₃₁ during a warm period, indicating significant inputs from the road dust and plant waxes. In fact, high-speed winds in warm period may uplift the road dust into the atmosphere in addition to plant waxes (Fig. 2c) in central Alaska. However, this is not the case in a cold period as evidenced by the almost negligible concentrations of C_{29} and C_{31} compared to a warm period.

Fatty acids ($C_{12:0}$ - $C_{32:0}$) including unsaturated fatty acids ($C_{14:1}$, $C_{16:1}$, $C_{18:n}$, $C_{20:1}$, $C_{22:1}$, and $C_{24:1}$) are detected in ambient aerosols in central Alaska. The molecular distributions of fatty acids are characterized by strong even-carbon number predominance with C_{max} at $C_{24:0}$ in both periods. However, in cold period, the molecular distribution of fatty acids showed a bimodal pattern with C_{max} at $C_{24:0}$ and $C_{16:0}$. A similar bimodal distributions were observed for mountainous (Fu et al., 2008) and remote marine aerosols (Kawamura et al., 2003)

with C_{max} at C_{16} and C_{24} . It was reported that high molecular weight $(\geq C_{20})$ fatty acids are derived from terrestrial higher plant waxes, while LMW fatty acids $(\leq C_{19})$ have multiple sources including vascular plants, microbes, phytoplankton and cooking activities (Fu et al., 2012; Kawamura et al., 2003; Schauer et al., 1996). Therefore, the sources of fatty acids are likely associated with terrestrial higher plant waxes in warm period, whereas fossil fuel combustion, such as diesel exhaust, and cooking activities are important sources in addition to plant emissions in cold period in central Alaska.

It was reported that methanesulfonate (MSA⁻) can be used as a specific tracer of biogenic sources such as terrestrial higher plants, microbes, and marine phytoplankton, etc. (Boreddy et al., 2018, 2015). In this study, MSA⁻ concentrations in cold period (mean: 0.004) were very low and its atmospheric abundances are five-time lower compared to the warm period. These results suggest that phytoplankton and microbe related sources of fatty acids are not significant in cold period. This point was further supported by the significant (p < 0.05) lower ratios of MSA⁻/EC during the cold period (Table 1). The MSA⁻/EC ratios were generally used to distinguish the relative contributions between biogenic vs. fossil fuel combustion sources. The lower ratios during cold period indicating the importance of combustion sources in central Alaska. On the other hand, C18:2 and C20:1 are the abundant species among all the detected unsaturated fatty acids in warm and cold periods, respectively. These unsaturated fatty acids are signatures of fresh biogenic inputs from terrestrial higher plants and microbial and/ or marine sources (Gagosian et al., 1981; Rudich et al., 2007).

Molecular distributions of normal fatty alcohols or n-alcohols (C8-



Fig. 3. Difference in the mean molecular distributions of (a) n-alkanes, (b) fatty acids, and (c) n-alcohols during warm and cold periods from central Alaska during June 2008 to June 2009.

 C_{30}) are characterized by even-carbon number predominance with C_{max} at C_{26} followed by C_{22} in warm period, while in cold period C_{max} at C_{22} followed by C_{24} in cold period. This trend is somehow similar to that of n-alkanes. It has been suggested that HMW ($\geq C_{20}$) n-alcohols are abundant in higher plant waxes and also can be emitted by biomass burning process (Fu et al., 2012; Ren et al., 2016; Wang et al., 2006) whereas LMW (< C20) n-alcohols are limited to soil microbes and marine biota (Fu et al., 2008). The predominance of high carbon number (C_{20} - C_{30}) suggests that n-alcohols are likely originated from higher plant waxes, biomass burning process and soil resuspention sources. However, their relative contributions could vary with time.

3.2. Temporal variations and sources

In order to better assess the contributions of biogenic and anthropogenic sources to lipid components, we present a couple of source signatures such as CPI and LMW/HMW ratios along with temporal variations of total concentrations of lipid components as shown in Fig. 4, while monthly mean variations are presented in Fig. 5. It has been reported that lipids are associated with the terrestrial higher plant origin when the CPI > 5, while CPI is close to 1 for anthropogenic inputs from fossil fuel combustions (Simoneit, 2004). Similarly, LMW/HMW ratio has been widely used to identify the source strengths in aerosols (Ren et al., 2016).

The total concentrations of n-alkanes in central Alaska showed

significant differences between warm and cold periods. We found that higher concentrations in warm period (range: $5.38-50.2 \text{ ng m}^{-3}$; mean: $17.5 \pm 11.4 \text{ ng m}^{-3}$) and their atmospheric abundances were more than twice higher than those in cold period $(1.33-14.8 \text{ ng m}^{-3})$; 8.35 ± 4.56 ng m⁻³). The CPI indices of n-alkanes ranged from 2.2 to 21 (11.4 \pm 4.5) in warm period while those ranged between 1.05 and 5.81 with a mean of 2.27 \pm 1.2 in cold period. The mean CPI in warm period is five times higher than that in cold period, suggesting an enhanced biogenic input from terrestrial higher plants in warm period. On the other hand, we found significantly higher LMW/HMW ratios in cold period than those in warm period. The ratios of LMW/HMW ranged from 0.71 to 4.09 (2.35) and 0.77 to 2.04 (1.26) in cold and warm periods, respectively. This inference suggests that anthropogenic sources, which are derived from the incomplete combustion of fossil fuel and petroleum residue or wood combustion for domestic heating, might be important sources for n-alkanes in cold period. The calculated concentration of fossil fuel derived n-alkanes were higher in cold period (mean: $6.35 \pm 4.5 \text{ ng m}^{-3}$) and lower in warm period $(4.2 \pm 3.3 \,\mathrm{ng}\,\mathrm{m}^{-3})$, however, we did not observe statistically significant differences (p > 0.05) in their atmospheric abundances.

We noticed that a significantly higher concentration of plant wax derived n-alkanes $(3.71-36.4 \text{ ng m}^{-3}; 13.2 \pm 8.6 \text{ ng m}^{-3})$ in warm period and their abundance was about seven times higher than that in cold period $(0.49-4.09 \text{ ng m}^{-3}; 2.0 \pm 0.9 \text{ ng m}^{-3})$. The percent of wax n-alkanes (%WNA) were higher in warm period (54–89%; 76 ± 8%)

Table 1

Summary of total concentrations (ng m $^{-3}$) and other parameters of lipid compounds in TSP aerosols collected from central Alaska for warm and cold periods during June 2008–June 2009.

	Warm per	iod (n = 16)		Cold period	l (n = 15)		Mann-Whitney U test				
	Avg	Sdtev	Max	Min	Avg	Sdtev	Max	Min	U value	Z Score	<i>p</i> -value
n-Alkanes (C ₁₉ -C ₃₅)											
Σn-Alkanes	17.5	11.4	50.2	5.38	8.35	4.56	14.8	1.33	1	-4.42	p < 0.05
CPI ^a	11.4	4.53	21.4	5.05	2.27	1.27	5.81	1.05	33	-2.94	p < 0.05
LMW/HMW ^b	1.26	0.39	2.04	0.77	2.35	1.07	4.09	0.71	48	-2.86	p < 0.05
Plant wax ^c	13.2	8.63	36.4	3.72	2.00	0.98	4.09	0.49	1	4.68	p < 0.05
Fossil fuel ^c	4.2	3.29	13.8	1.14	6.35	4.53	12.9	0.84	89	-1.21	p > 0.05
%WNA ^d	75.9	7.98	88.9	54.5	30.7	18.7	66.5	6.94	1	4.68	p < 0.05
ACL ^e	26.1	0.37	26.8	25.5	25.8	0.56	26.9	25.1	69	1.99	p < 0.05
Fatty acids (C ₁₂ -C ₃₂)											
$\Sigma(C_{12}-C_{32})$	82.2	103	438	18.9	48.7	32.8	98.4	7.69	101	0.73	p > 0.05
Σ even (C _{14:1} -C _{24:1})	5.72	3.58	15.4	2.26	2.54	1.85	5.86	0.22	48	2.82	p < 0.05
CPI	8.03	2.68	12.7	2.58	9.63	1.32	11.7	6.50	102	0.69	p > 0.05
LMW/HMW	1.19	1.75	7.57	0.34	1.28	0.60	2.77	0.51	64	-2.19	p < 0.05
$C_{18:1}/C_{18:0}$	0.13	0.12	0.55	0.04	0.08	0.15	0.60	0.02	34.5	3.35	p < 0.05
$C_{16:1}/C_{16:0}$	0.05	0.04	0.18	0.01	0.05	0.02	0.10	0.02	89	-1.20	p > 0.05
C _{18:0} /C _{16:0}	0.69	0.41	1.82	0.13	0.51	0.04	0.57	0.45	79	1.60	p > 0.05
C_{sat}/C_{unsat}^{f}	10.3	8.64	37.4	2.38	19.9	10.7	45.9	6.76	41	-3.10	p < 0.05
ACL	24.1	0.75	26.4	23.1	23.7	0.39	24.8	23.3	68.5	2.01	p < 0.05
n-Alcohols (C8-C30)											
Σn-Alcohols	33.7	24.51	107	10.0	12.4	5.48	19.2	3.92	38	3.22	p < 0.05
CPI	7.38	1.97	11.1	3.18	6.47	1.83	8.96	3.23	91	1.12	p > 0.05
LMW/HMW	0.61	0.41	1.68	0.20	1.20	0.47	1.85	0.49	39	-3.18	p < 0.05
ACL	25.5	0.76	27.8	24.5	24.6	0.75	26.1	23.4	48	2.82	p~<~0.05
WSOC/OC	0.45	0.09	0.57	0.32	0.59	0.09	0.80	0.48	21.5	-3.87	P < 0.05
nss-K ⁺ /EC	0.09	0.03	0.14	0.03	0.04	0.03	0.10	0.0	34	3.37	P < 0.05
MSA ⁻ /EC	0.05	0.03	0.12	0.0	0.01	0.01	0.02	0.0	18.5	3.99	P < 0.05

^a Carbon preference index, CPI = Σ odd (C₂₁-C₃₅)/ Σ even (C₂₀-C₃₄) for n-alkanes; CPI = Σ even (C_{20:0}-C_{32:0})/ Σ odd (C_{21:0}-C_{31:0}) for fatty acids; CPI = Σ even (C₂₀-C₃₂)/ Σ odd (C₂₁-C₃₁) for n-alcohols.

^b LMW/HMW: low molecular weight/high molecular weight.

^c Plant wax n-alkanes: the excess odd homologue – adjacent even homologues average, and the difference from total n-alkanes is fossil fuel or petroleum derived amount.

 d Wax n-alkane percent, WNA% = ΣC_n – 0.5(C_{n-1} + C_{n+1})/\Sigma C_n-alkanes x 100%.

^e Average chain length, ACL, weight-averaged odd numbered carbon atoms of higher plants ($\geq C_{23}$).

 $\label{eq:constraint} {}^{\rm f} \ C_{sat}/C_{unsat} = (C_{14:0} \ + \ C_{16:0} \ + \ C_{18:0} \ + \ C_{20:0} \ + \ C_{22:0} \ + \ C_{24:0})/C_{14:1} \ + \ C_{16:1} \ + \ C_{18:n} \ + \ C_{20:1} \ + \ C_{22:1} \ + \ C_{24:1}).$

and their abundances were more than twice than those in cold period (7–66%; 31 \pm 19%). These results again suggest that n-alkanes were most likely derived from higher plant waxes in warm period in central Alaska.

The ACL index for n-alkanes varied from 25.5 to 26.8 (mean: 26.1 \pm 0.4) in warm period while these were 25.1–26.9 (25.8 \pm 0.5) in cold period; little variation in this index implies biogenic activities from higher plants as the major source of n-alkanes (Jeng, 2006). In addition, road dust is also a significant source for n-alkanes as evidenced by a significant higher concentration of C₂₉ in warm period (0.23 ng m⁻³ in warm period and 0.01 ng m⁻³ in cold period) because C₂₉ n-alkane is a good marker for road dust suspension (Kang et al., 2016; Yadav et al., 2013).

Temporal variations of fatty acids along with source indices are shown in Fig. 4b. Total concentrations of normal fatty acids ranged from 19 to 438 ng m⁻³ (mean: 82.2 \pm 103 ng m⁻³) in warm period and from 7 to 98 ng m⁻³ (48.7 \pm 98 ng m⁻³) in cold period. The CPI indices of fatty acids varied from 2.58 to 12.7 in warm period and 6.5 to 11.7 in cold period. Although there is no significant difference (p > 0.05) in the CPI indices of fatty acids between the cold and warm periods, we noticed that most of the samples showed CPI > 5, implying that fatty acids in central Alaska are likely derived from terrestrial higher plant wax (Fu et al., 2010a). The mean ratio of LMW/HMW fatty acids showed significantly (p < 0.05) higher in cold period (1.28 \pm 0.6) than that in warm period (1.19 \pm 1.7), suggesting a dominance of LMW fatty acids during cold period. LMW fatty acids have several sources including vascular plants, microbial, marine phytoplankton and cooking emissions (Fu et al., 2010a; Rogge et al., 1991).

It has been suggested that fatty acid ratio $C_{18:0}/C_{16:0}$ can be used to estimate the source types (Ren et al., 2016; Rogge et al., 2006). For example, C18:0/C16:0 values are lower than 0.25 for aerosols associated with foliar vegetation combustion, waxy leaf surface abrasions, and wood smoke; values in the range from 0.25 to 5.0 are marked for fossil fuel combustions including petroleum and diesel exhausts; values in the interval of 0.5-1.0 are signature for cooking emissions and road dust (Ren et al., 2016; Rogge et al., 2006). In this study, $C_{18:0}/C_{16:0}$ ratios showed mean values of 0.69 \pm 0.41 (range: 0.13–1.82) and 0.51 ± 0.04 (0.45–0.57) in warm and cold periods, respectively. It should be noted that the range of $C_{18:0}/C_{16:0}$ ratios in cold period was very narrow compared to warm period and moreover, the standard deviation of the mean value in cold period was about ten times lower than that of warm period. These results suggest that fossil fuel combustion and cooking emissions are important for fatty acids in cold period while road dust, cooking and vehicular emissions are important in warm period in addition to higher plant emissions. Plant tissues are enriched with abundant fatty acids that can be emitted from biomass burning, thus, biomass burning process can emit a significant amount of fatty acids into the atmosphere (Fu et al., 2012; Simoneit, 2002).

It should be note that although the mean value (0.51 ± 0.04) of $C_{18:0}/C_{16:0}$ ratios in cold period is very close to the interval of 0.5–1.0 (signature for cooking emissions and road dust), most data points $(C_{18:0}/C_{16:0}$ ratios) were fallen under the value of 5.0, suggesting an importance of combustion sources in cold period rather than road dust. In addition, C_{29} has been suggested as a specific biomarker for road dust that contains automobile exhausts and surface deposited plant litter (Yadav et al., 2013; Kang et al., 2016). In this view, we found negligible



Fig. 4. Temporal variations in the total concentrations of aliphatic lipids detected in the central Alaskan aerosols. Warm and cold periods are indicated by light blue and pink colors, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

concentrations of C_{29} in a cold period compared to those of the warm period. Based on the above discussions, road dust could be omitted from the sources of fatty acids in cold period.

Unsaturated fatty acids are suggested to be good indicators for fresh biogenic inputs from terrestrial higher plants and microbial/marine origins (Yang et al., 2016). Because of their rapid oxidation and photochemical degradation, they can be used as a proxy to estimate the aging of OA in the atmosphere (Gagosian et al., 1982; Kawamura and Gagosian, 1987; Simoneit and Mazurek, 1982). In this study, total concentrations of unsaturated fatty acids ranged from 2.26 to 15.4 (5.72 ± 3.58) and from 0.22 to 5.86 (2.54 \pm 1.85) in warm and cold periods, respectively. We found a significantly higher concentration in warm period and their atmospheric abundances were two times higher than those in cold period, suggesting fresh biogenic inputs in warm period. It has also been suggested that $C_{18:1}/C_{18:0}$ and $C_{16:1}/C_{16:0}$ ratios can be used for studying reactivity and aging of organic aerosols in the atmosphere: lower values indicate the inputs of aged OA from anthropogenic sources while higher values indicate linked to terrestrial higher plant emissions (Bendle et al., 2007). In this view, we found significantly higher values (0.04–0.55; 0.13 \pm 0.12) of C_{18:1}/C_{18:0} in warm period than in cold period (0.02–0.60; 0.08 \pm 0.15). This result suggests that enhanced aged organic aerosols in cold period at central Alaska probably due to the temperature inversion mechanism.

Because of the subarctic region, Fairbanks experiences very long

cold winters and short warm summers, in which much of the precipitation occurs (Fig. 2). In addition to very cold temperatures and high pressure air, the air shed shaped topography of Fairbanks makes its atmospheric situation more favourable for temperature inversions in winter. As a sequence, trapping of air pollutants, which come from combustion-derived anthropogenic sources in the valley for days to weeks, often leads to the formation of ice fog. Therefore, temperature inversion may likely cause the aged organic aerosols in cold period. In this view, we found significantly higher WSOC/OC ratios (a proxy for chemical aging) in cold period (0.48-0.80; 0.59) than warm period (0.32-0.57; 0.45), implying more aged aerosols in cold period. We also found significantly higher ratios of C_{sat}/C_{unsat} in cold periods (6.76-45.9; 19.9) than those in warm period (2.38-37.4; 10.3) in central Alaska, suggesting that aged anthropogenic and fresh biogenic emissions are important sources for fatty acids in cold and warm periods, respectively.

Fig. 4c presents the temporal variations in the total concentrations of n-alcohols in ambient aerosols at Alaska ranged from 10 ng m^{-3} to 107 ng m^{-3} (mean: 33.7 ng m^{-3}) and 3.92 ng m^{-3} to 19.2 ng m^{-3} (12.4 ng m⁻³) in warm and cold periods, respectively. We found that significantly higher concentrations in warm period and their atmospheric abundances were about three times to those in cold period. It has been suggested that HMW n-alcohols (> C₂₀) are abundant in higher plant waxes and can also be emitted from biomass burning while

Fig. 5. Monthly variations in the total concentrations of aliphatic lipids detected in the central Alaskan aerosols.

LMW n-alcohols (< C_{20}) are limited to soil microbes and marine biota (Fu et al., 2009; Simoneit, 2002). In this study, the CPI values of nalcohols showed no significant difference between the two periods, however, LMW/HMW showed significantly higher values (0.49–1.85; 1.20) in cold period than in warm period (0.20–1.68; 0.61). Further, nss-K⁺/EC ratios showed significantly higher values in warm period (0.03–0.14; 0.09) than in cold period (0–1.0; 0.04). These results demonstrate that higher plant waxes, biomass burning emissions and soil resuspension are the major sources of n-alcohols from central Alaska in warm period while combustion derived anthropogenic emissions are the important sources in cold period.

3.3. Relative abundances of terrestrial biomarkers

To further explore the sources of lipid components in central Alaska, we present relative abundances (%) of terrestrial biomarkers such as nalkanes (C_{25-35}), fatty acids (C_{20-32}), and n-alcohols (C_{20-30}) using a ternary diagram (Fig. 6). The results show that higher abundance of fatty acids (56–77%) on cold period while a higher abundance of nalkanes (7–27%) and n-alcohols (17–53%) are occurring on warm period. Although the linear regression correlations were strong among three biomarkers, we found higher correlation coefficients in warm period ($R^2 = 0.78$ –0.97) than those in cold period (0.78–0.83), suggesting that origin of different terrestrial biomarkers from similar sources is more obvious in warm period. As seen in Fig. 6, most of the aerosol samples fell into the upper part of the triangle, suggesting the higher abundance of long-chain fatty acids in central Alaska (Kawamura et al., 2003), particularly in cold period. The distribution of terrestrial biomarkers in central Alaska is different from those mountainous (category A), urban (categories B and C), western Pacific and Southern Ocean aerosols (category D), implying that the sources/origins of terrestrial organic aerosols are probably different in central Alaska.

Kawamura et al. (2003) reported terrestrial biomarkers in marine aerosol samples collected at Chichijima island in the western North Pacific during 1991–1993. They demonstrated that terrestrial higher plant emissions, which were transported from Asian continent, are major sources of terrestrial biomarkers in westerly winds, while aerosols collected under the easterly wind regime may be involved with the specific vegetation in the source region whose biological situation may be different from Asian continent. The relative abundances are those samples were reported as categories E and F in Fig. 6. In this view, we noticed that the distributions of these plots in warm and cold periods are overlapped with categories E and F of Chichijima aerosols, which were collected under westerly and easterly wind regimes, respectively. This observation suggests that terrestrial higher plant emissions should

Fig. 6. Triangular plot of relative abundance of terrestrial biomarkers: n-alkanes (C_{25} - C_{33}), fatty acids (C_{20} - C_{32}), and n-alcohols (C_{20} - C_{32}) in the aerosols collected from the Alaska. The mountainous biomass burning influenced aerosols collected at the summit of Mt. Tai, North China fall in category A (Fu et al., 2008) indicated by yellow circle. Beijing aerosols collected during winter fall into the category B (Ren et al., 2016) (purple). Springtime aerosols from New Delhi, India fall into the category C (Kang et al., 2016) (green). Marine aerosols collected at western Pacific fall in category D (Bendle et al., 2007) (red) whereas marine aerosols collected at Chichijma island in the western North Pacific are fall into the category E and F for winter/spring and summer (Kawamura et al., 2003) (blue colored solid and dotted line), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

be significant sources of terrestrial biomarkers in central Alaska, especially in warm period. We further noticed that some data points in warm period may fall into the category A, which were collected at the summit of Mt. Tai under intense field burning (Fu et al., 2008), suggesting that importance of biomass burning emissions such as wildfire in warm period in central Alaska.

It should be noted that the sources of terrestrial biomarkers in this study could be explained by not only the ternary plots but also many source indices such as CPI, HMW/LMW ratios, ACL, and inorganic and organic ratios. Moreover, many previous studies were used this ternary diagram to distinguish the sources of biomarkers at different atmospheric aerosol sampling sites (urban, biomass burning, dust and marine aerosols) as explained above. Therefore, it is reasonable to make a ternary plot to evaluate relative abundances of terrestrial biomarkers by comparing with other sites.

3.4. Comparison with other studies

Due to the different climatic/geographical situations between Alaska and Asian regions, molecular composition and biogenic emission rate of organic aerosols (for example, fatty acids) may be different in both the regions, particularly during the winter season, although the sources may be common. Fatty acids are primarily associated with emissions from plant leaves and biological activities in the source regions. Further, in this study, most of our interpretation is based on the diagnostic mass ratios and source indices (CPI, ACL, etc.). The ratios can be used as more conservative tracers rather than the absolute concentrations because all chemical species undergo similar degradation and formation processes of organic aerosols. Therefore, it is reasonable to compare the sources of lipids in central Alaska with Asian sites and around the globe.

Table 2 summarizes the comparison of total concentrations of lipid class components and their source indices (C_{max} , CPI, ACL, etc.) in aerosols collected from central Alaska with other sites around the globe. As seen in Table 2, it is obvious that the total concentrations of all three lipid components (n-alkanes, fatty acids and n-alcohols) in central Alaskan aerosols were several times lower than the urban aerosols (Fu et al., 2010b; Kang et al., 2016; Ren et al., 2016; Wang and Kawamura, 2005), biomass burning influenced mountainous aerosols (Fu et al., 2008) and higher than the western North Pacific, Arctic Ocean and Canadian high arctic (Alert) aerosols (Fu et al., 2009, 2013; Kawamura et al., 2003). These results suggest that the origin and strength of lipid

Table 2

Comparison of lipid class compound concentrations (ng m⁻³) and different source indices from this study with those around the globe.

Location	n-alkanes (ng m ⁻³)						Fatty acids (ng m ⁻³)				n-alcohols (ng m ⁻³)				References
	Concen.	C _{max}	ACL	CPI	Fossil fuel	%WNA	Concen.	C _{max}	CPI	ACL	Concen.	C _{max}	CPI	ACL	
Fairbanks, Alaska															
Cold period	8.35	C ₂₅	25.8	2.27	6.35	30.7	48.7	C _{24:0}	9.6	24.1	12.4	C ₂₆	6.4	24.6	Present study
Warm period	17.5	C ₂₅	26.1	11.4	4.2	76	82.2	C _{24:0}	8	23.7	33.7	C ₂₂	7.4	25.5	
Beijing, China															
Daytime	262	C ₂₃		1.6		19	733	C _{16:0}	5		109	C ₂₆	4.1		Ren et al., 2016
Nightime	472	C ₂₃		1.4		15	1010	C _{16:0}	4.7		190	C ₂₆	4.8		
New Delhi, India															
Haze	293	C ₂₉	28.3	1.4	249	15	1458	C _{14:0}	18.5		288	C_{18}	8.9		Kang et al., 2016
non-Haze	230	C ₂₉	28.4	1.7	186	19	1008	C _{16:0}	10.8		337	C ₁₈	10.8		
Dust storm	681	C ₂₉	27.8	1.2	631	7	617	C _{16:0}	9.1		289	C18	-		
Chennai, India															
Winter	141	C ₂₉		1.56			302	C _{16:0}	3.99		67.9	C ₂₈	9.75		Fu et al., 2010b
Summer	187	C ₂₉		1.52			504	C _{16:0}	3.61		70.4	C ₂₈	10.9		
Nanjing, China															
Summer –day	54	C ₂₉		3.46			210	C _{30:0}	6.8		86	C ₂₆	16.9		Wang and Kawamura, 2005
Summer –night	82	C ₂₉		2.03			316	C _{16:0}	6.3		97	C ₂₆	9.8		
Winter –day	172	C ₂₃		1.34			245	C _{16:0}	7.6		74	C ₂₆	13.3		
Winter –night	278	C ₂₃		1.16			338	C _{16:0}	7.6		120	C ₂₆	19.1		
Mt. Tai, China															
Daytime	161	C ₂₇		4.42			262	$C_{16:0}/C_{28:0}$	6.04		249	C ₂₈	25.6		Fu et al., 2008
Nighttime	194			4.63			287		5.53		352		22.8		
Chichijima, Japan	1.7	C ₂₉	29–31	4.5			14	$C_{16:0}/C_{24:0}$	-	24–28	2.0	C ₂₆	-	26–28	Kawamura et al., 2003
Arctic Ocean	0.14-4.5	C ₂₇		1.5-2				C _{16:0}	2–8			C14	3–18		Fu et al., 2013
Alert, Arctic	0.2–2.16	C ₂₁		1.2–2			0.7–2.4	C _{16:0}	2–8		0.4–2.0	C ₂₈	2.7–12		Fu et al., 2009

components are probably different and depend on the environmental and/or geographic conditions.

It should be noted that although there is no significant difference in the CPI indices of fatty acids and n-alcohols, we found a significant difference in the CPI values of n-alkanes between warm and cold period, indicating the different sources of n-alkanes in warm and cold periods. The mean CPI value of n-alkanes in cold period is relatively close to that of urban aerosols but lower than Chichijima and Mt. Tai aerosols, suggesting that incomplete combustions of fossil fuel and petroleum residue are important sources for n-alkanes in cold period. On the other hand, the mean CPI value in warm period is several times higher than those in other sites, demonstrating that terrestrial higher plant emissions are the main sources of n-alkanes in warm period in central Alaska. The %WNA values in both periods in central Alaska were several times higher than those of urban aerosols in China and India, further suggesting the importance of higher plant emissions for nalkanes, especially in warm period.

4. Conclusions

In this study, we determined lipid class compounds in atmospheric aerosols at central Alaska over a one year period from June 2008 to June 2009. As the subarctic climate in Alaska, whole sampling period was divided into warm (May to late September) and cold (late September to early May) periods. Molecular distribution was characterized by the predominance of C_{25} for n-alkanes and $C_{24:0}$ for fatty acids in both periods. However, we noticed a difference in molecular distribution of n-alcohols between warm summer and cold winter, which are characterized by the predominance of C_{22} in summer while C_{26} in winter period.

Except for fatty acids, n-alkanes and n-alcohols showed significant difference in their concentrations between warm and cold periods with higher concentrations in warm period. CPI values of n-alkanes showed significantly higher values in warm (range: 5.0 to 21; mean: 11.4) than in cold period (1.0–5.8; 2.35), emphasizing a larger contribution of terrestrial higher plant waxes in warm period while anthropogenic emissions are important in cold period. This inference is further supported by the significantly higher percent (\sim 75%) of wax n-alkanes and fossil fuel (\sim 70%) in warm and cold period, respectively.

We found significantly higher $C_{18:1}/C_{18:0}$ ratios in warm period (0.04–0.55; 0.13 ± 0.12) and lower ratios in cold period (0.02–0.60; 0.08 ± 0.15), indicating the fresh biogenic emissions in summer and aged anthropogenic aerosols in winter. Further, low-to-high molecular weight (LMW/HMW) ratios of n-alcohols showed significantly higher values (0.49–1.85; 1.20) in cold period than those in warm period (0.20–1.68; 0.61), emphasizing the higher plant waxes and biomass burning from wildfires are the important sources in warm period while combustion derived anthropogenic emissions are major sources in cold period in central Alaska. All these results have important implications towards the regional radiative balance calculations, particularly in the subarctic Alaska.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.

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References

- Bendle, J., Kawamura, K., Yamazaki, K., 2006. Seasonal changes in stable carbon isotopic composition of n-alkanes in the marine aerosols from the western North Pacific: implications for the source and atmospheric transport. Geochem. Cosmochim. Acta 70, 13–26.
- Bendle, J., Kawamura, K., Yamazaki, K., Niwai, T., 2007. Latitudinal distribution of terrestrial lipid biomarkers and n-alkane compound-specific stable carbon isotope ratios in the atmosphere over the western Pacific and Southern Ocean. Geochim. Cosmochim. Acta 71, 5934–5955.
- Bergmann, R., Ludbrook, J., Spooren, W.P.J.M., 2000. Different outcomes of the Wilcoxon—Mann—Whitney test from different statistics packages. Am. Statistician 54, 72–77.
- Boreddy, S.K.R., Haque, M.M., Kawamura, K., 2018. Long-term (2001-2012) trends of carbonaceous aerosols from a remote marine island in the western North Pacific: an outflow region of Asian pollutants. Atmos. Chem. Phys. 8, 1291–1306.
- Boreddy, S.K.R., Kawamura, K., 2015. A 12-year observation of water-soluble ions in TSP aerosols collected at a remote marine location in the western North Pacific: an outflow region of Asian dust. Atmos. Chem. Phys. 15, 6437–6453.
- Brown, S.G., Herckes, P., Ashbaugh, L., Hannigan, M.P., Kreidenweis, S.M., Collett, J.L., 2002. Characterization of organic aerosol in Big Bend National Park, Texas. Atmos. Environ. 36, 5807–5818.
- Fang, M., Zheng, M., Wang, F., To, K.L., Jaafar, A.B., Tong, S.L., 1999. The solvent-extractable organic compounds in the Indonesia biomass burning aerosols – characterization studies. Atmos. Environ. 33, 783–795.
- Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2001. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. Environ. Sci. Technol. 35, 2665–2675.
- Fu, P., Kawamura, K., Barrie, L.A., 2009. Photochemical and other sources of organic compounds in the Canadian high Arctic aerosol pollution during winter-spring. Environ. Sci. Technol. 43, 286–292.
- Fu, P., Kawamura, K., Chen, J., Charriere, B., Sempere, R., 2013. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation. Biogeosciences 10, 653–667.
- Fu, P., Kawamura, K., Chen, J., Li, J., Sun, Y.L., Liu, Y., Tachibana, E., Aggarwal, S.G., Okuzawa, K., Tanimoto, H., Kanaya, Y., Wang, Z.F., 2012. Diurnal variations of organic molecular tracers and stable carbon isotopic composition in atmospheric aerosols over Mt. Tai in the North China Plain: an influence of biomass burning. Atmos. Chem. Phys. 12, 8359–8375.
- Fu, P., Kawamura, K., Kanaya, Y., Wang, Z., 2010a. Contributions of biogenic volatile organic compounds to the formation of secondary organic aerosols over Mt. Tai, Central East China. Atmos. Environ. 44, 4817–4826.
- Fu, P., Kawamura, K., Okuzawa, K., Aggarwal, S.G., Wang, G., Kanaya, Y., Wang, Z., 2008. Organic molecular compositions and temporal variations of summertime mountain aerosols over Mt. Tai, North China Plain. J. Geophys. Res. Atmos. 113, D19107. http://dx.doi.org/10.1029/2008JD009900.
- Fu, P., Kawamura, K., Pavuluri, C.M., Swaminathan, T., Chen, J., 2010b. Molecular characterization of urban organic aerosol in tropical India: contributions of primary emissions and secondary photooxidation. Atmos. Chem. Phys. 10, 2663–2689.
- Gagosian, R.B., Peltzer, E.T., Zafiriou, O.C., 1981. Atmospheric transport of continently derived lipids to the tropical North Pacific. Nature 291, 312–314.
- Gagosian, R.B., Zafiriou, O.C., Peltzer, E.T., Alford, J.B., 1982. Lipid in aerosols from the tropical North Pacific: temporal variability. J. Geophys. Res. 87, 11133–11144.
- Haque, M.M., Kawamura, K., Kim, Y., 2016. Seasonal variations of biogenic secondary organic aerosol tracers in ambient aerosols from Alaska. Atmos. Environ. 130, 95–104.
- Jeng, W.-L., 2006. Higher plant n-alkane average chain length as an indicator of petrogenic hydrocarbon contamination in marine sediments. Mar. Chem. 102, 242–251.
- Kang, M., Fu, P., Aggarwal, S.G., Kumar, S., Zhao, Y., Sun, Y., Wang, Z., 2016. Size distributions of n-alkanes, fatty acids and fatty alcohols in springtime aerosols from New Delhi, India. Environ. Pollut. 219, 957–966.
- Kawamura, K., Gagosian, R.B., 1987. Implications of ω-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids. Nature 325, 330–332.
- Kawamura, K., Ishimura, Y., Yamazaki, K., 2003. Four years' observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific. Global Biogeochem. Cycles 17, 1003. http://dx.doi.org/10.1029/2001GB001810.
- Lyu, Y., Xu, T., Yang, X., Chen, J., Cheng, T., Li, X., 2017. Seasonal contributions to sizeresolved n-alkanes (C8–C40) in the Shanghai atmosphere from regional anthropogenic activities and terrestrial plant waxes. Sci. Total Environ. 579, 1918–1928.
- Marzi, R., Torkelson, B.E., Olson, R.K., 1993. A revised carbon preference index. Org. Geochem. 20, 1303–1306.
- Pietrogrande, M.C., Mercuriali, M., Perrone, M.G., Ferrero, L., Sangiorgi, G., Bolzacchini, E., 2010. Distribution of n-alkanes in the Northern Italy aerosols: data handling of GC-MS signals for homologous series characterization. Environ. Sci. Technol. 44, 4232–4240.
- Ren, L., Fu, P., He, Y., Hou, J., Chen, J., Pavuluri, C.M., Sun, Y., Wang, Z., 2016. Molecular distributions and compound-specific stable carbon isotopic compositions of lipids in wintertime aerosols from Beijing. Sci. Rep. 6, 27481.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1991. Source of fine organic aerosols: 1. Charbroilers and meat cooking operations. Environ. Sci. Technol. 25, 1112–1125.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources

S.K.R. Boreddy et al.

of fine organic aerosol .4. Particulate abrasion products from leaf surfaces of urban plants. Environ. Sci. Technol. 27, 2700–2711.

- Rogge, W.F., Medeiros, P.M., Simoneit, B.R.T., 2006. Organic marker compounds for surface soil and fugitive dust from open lot dairies and cattle feedlots. Atmos. Environ. 40, 27–49.
- Rudich, Y., Donahue, N.M., Mentel, T.F., 2007. Aging of organic aerosol: bridging the gap between laboratory and field studies. Annu. Rev. Phys. Chem. 58, 321–352.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 1. C₁ through C₂₉ organic compounds from meat charbroiling. Environ. Sci. Technol. 33, 1566–1577.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. Atmos. Environ. 30, 3837–3855.
- Shakya, K.M., Peltier, R.E., 2013. Investigating missing sources of sulfur at Fairbanks, Alaska. Environ. Sci. Technol. 47, 9332–9338.
- Simoneit, B.R.T., 1984. Organic matter of the troposphere-III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States. Atmos. Environ. 18, 51–67.
- Simoneit, B.R.T., 2002. Biomass burning-a review of organic tracers for smoke from incomplete combustion. Appl. Geochem. 17, 129–162.
- Simoneit, B.R.T., 2004. Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign. J. Geophys. Res. 109.
- Simoneit, B.R.T., Elias, V.O., 2000. Organic tracers from biomass burning in atmospheric particulate matter over the ocean. Mar. Chem. 69, 301–312.
- Simoneit, B.R.T., Elias, V.O., 2001. Detecting organic tracers from biomass burning in the atmosphere. Mar. Pollut. Bull. 42, 805–810.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the troposphere-II. Natural background of biogenic lipid matter in aerosols over the rural western United States.

- Atmos. Environ. 16, 2139-2159.
- Simoneit, B.R.T., Sheng, G.Y., Chen, X.J., Fu, J.M., Zhang, J., Xu, Y.P., 1991. Molecular marker study of extractable organic-matter in aerosols from urban areas of China. Atmos. Environ. Part A 25, 2111–2129.
- Tang, X.L., Bi, X.H., Sheng, G.Y., Tan, J.H., FU, J.M., 2006. Seasonal variation of the particle size distribution of n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in urban aerosol of Guangzhou, China. Environ. Monit. Assess. 117, 193–213.
- Tanski, G., Lantuit, H., Ruttor, S., Knoblauch, C., Radosavljevic, B., Strauss, J., Wolter, J., Irrgang, A.M., Ramage, J., Fritz, M., 2017. Transformation of terrestrial organic matter along thermokarst-affected permafrost coasts in the Arctic. Sci. Total Environ. 581–582, 434–447.
- Wang, G., Kawamura, K., 2005. Molecular characteristics of urban organic aerosols from Nanjing: a case study of a mega-city in China. Environ. Sci. Technol. 39, 7430–7438.
- Wang, G., Kawamura, K., Lee, S., Ho, K.F., Cao, J.J., 2006. Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities. Environ. Sci. Technol. 40, 4619–4625.
- Ward, T., Trost, B., Conner, J., Flanagan, J., Jayanty, R.K.M., 2012. Source apportionment of PM_{2.5} in a Subarctic Airshed - Fairbanks, Alaska. Aerosol Air Qual. Res. 12, 536–543.
- Ware, D., Lewis, J., Hopkins, S., Boyer, B., Noonan, C., Ward, T., 2013. Sources and perceptions of indoor and ambient air pollution in rural Alaska. J. Community Health 38, 773–780.
- Yadav, S., Tandon, A., Attri, K.A., 2013. Monthly and seasonal variations in aerosol associated n-alkane profiles in relation to meteorological parameters in New Delhi, India. Aerosol Air Qual. Res. 13, 287–300.
- Yang, F., Kawamura, K., Chen, J., Ho, K., Lee, S., Gao, Y., Cui, L., Wang, T., Fu, P., 2016. Anthropogenic and biogenic organic compounds in summertime fine aerosols (PM2.5) in Beijing, China. Atmos. Environ. 124 (Part B), 166–175.