

Concentrations and sources of carbonaceous aerosol in the atmosphere of Summit, Greenland

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ABSTRACT

High-volume PM_{2.5} samples were collected at Summit, Greenland for approximately six months from late May through December of 2006. Filters were composited and analyzed for source tracer compounds. The individual organic compounds measured at Summit are orders of magnitude smaller than concentrations measured at other sites, including locations representative of remote oceanic, and remote and urban continental aerosol. The measured tracers were used to quantify the contribution of biomass burning (0.6–0.9 ng C m⁻³), vegetative detritus (0.3–0.9 ng C m⁻³), and fossil fuel combustion (0.1–0.8 ng C m⁻³) sources, 4% of OC total, to atmospheric organic carbon concentrations at the remote location of Summit, Greenland. The unapportioned organic carbon (96%) during the early summer period correlates well with the fraction of water soluble organic carbon, indicating secondary organic aerosol as a large source of organic carbon, supported by the active photochemistry occurring at Summit. To the author's knowledge, this paper represents the first source apportionment results for the polar free troposphere.

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1. Introduction

The Arctic environment is thought of as one of the most pristine locations on earth, however, natural and/or anthropogenic pollution originating from populated and more polluted regions in the northern hemisphere have been shown to influence atmospheric concentrations in the Arctic (Quinn et al., 2008; Law and Stohl, 2007). Increasing pollution in the Arctic has become a topic of research interest, starting in the mid-1950s with the discovery of the springtime atmospheric pollution phenomenon known as Arctic haze (Barrie, 1986). Since then a number of studies have been done to characterize atmospheric pollution in the Arctic, mostly focusing on black carbon (Eleftheriadis et al., 2009; Sharma et al., 2006; Sharma et al., 2004; Bodhaine, 1995; Hansen et al., 1989), and aerosol optical properties (Clarke et al., 1984; Yamanouchi et al., 2005). Even now however, there is additional concern for the susceptibility of the Arctic to pollution from long range transport, because of its location in the northern hemisphere where the concentration of atmospheric pollutants is higher than in the

southern hemisphere, even in remote locations. Levels of black carbon measured in the Arctic were discovered to be two orders of magnitude greater than those recorded in the Antarctic (Hansen and Nazarenko, 2004). However, few studies have characterized the particulate organic component of the aerosol in the Arctic. The studies that have been done typically focus on one compound class, such as polycyclic aromatic hydrocarbons (PAHs) (Patton et al., 1991) or acids (Dibb and Arsenault, 2002; Narukawa et al., 2002), or on gas-phase organic species (Anderson et al., 2008; Dibb and Arsenault, 2002; Dibb et al., 1994, 1996; Jacobi et al., 2004; Sumner and Shepson, 1999). Recently, the elemental and organic carbon concentrations in the aerosol were measured by our collaborators at Summit, Greenland (Hagler et al., 2007). Here we conducted 6 months of sampling (May–December 2006) of the aerosol at Summit, which was analyzed for a variety of individual organic compounds. The characterization of the organic carbon component of the aerosol can be very useful for identifying possible sources of the aerosol using molecular markers. Molecular markers are species characteristic of a specific type of emission source, which along with distinguishable compound distribution patterns, can be used to apportion sources to aerosol samples (Simoneit, 1999). In order to better understand the sources impacting the Arctic during different time periods, this paper uses a receptor-based chemical mass balance model to determine possible sources contributing to the organic carbon at Summit, Greenland.

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2. Experimental

2.1. Filter sample collection

A high-volume sampler (Thermo Scientific, PM_{2.5}) was located at Summit, Greenland (72°N, 38°W, 3200 m elevation) from May through December 2006. Filter samples (Pall Gelman quartz fiber filters 8 × 10 inches) were collected from May 27 to December 28, 2006 in the designated 'clean air sector' of the research camp. Prior to sampling, the filters were ashed at 475° Celsius for 8 h. Filters were stored frozen, in ashed foil in sealed plastic bags before and after sampling. The clean air sector of camp is located to the south of the research station as wind directions are generally southerly (Hagler et al., 2008). The sampler was connected to a sector control system which would stop collection when the wind direction originated from camp, a possible source of contamination. On average, the sector control system results in approximately 20% of sampling time lost due to wind direction or stagnant wind conditions (Hagler et al., 2008). In addition, a specially designed Hepa filter unit was attached to the exhaust to remove any possible contamination from the carbon brushes in the pump motor. Each filter was collected for 160 h (on average) at a flow rate of 1000 lpm to ensure enough particulate matter accumulation on the filter. Field blanks, prepared, stored, and transported with the sampled filters, were periodically loaded into the high volume sampler and removed without any air being pumped through the filters.

2.2. Filter sample analysis

Filters were composited based on aerosol OC loadings and sample time into four time periods, each representing just over one month, ensuring enough extractable material. One filter was removed because of visible darkening of the sampled area and extracted separately. Each filter composite was spiked with 200 µl of internal standard, which contained deuterium-labeled compounds in a 2:1 benzene:isopropyl alcohol solution for quantification of compounds, and extracted by sonication; twice with 500 ml dichloromethane (DCM) and once with 500 ml methanol, for 10 min each. The sequential extractions were combined in a round-bottom flask for concentration by rotary evaporation to a volume of approximately 5 ml. After concentration the extract was transferred to a PTFE filter equipped syringe and filtered into a pre-cleaned test tube, followed by two 1 ml rinses of 50/50 DCM/methanol solvent mix. The extract was then further reduced in volume by a stream of nitrogen gas to 200 µl. Field blanks were composited to parallel the samples and analyzed with the same procedure. A parallel filter composite of lab blanks was spiked with particulate matter standards in addition to the internal standard for calculation of compound recoveries. The extracts were analyzed by GC-MS.

The high-volume filters were composited as follows, early summer (5/27/06–7/8/06), late summer (7/9/06–8/21/06), fall (8/23/06–10/4/06), and early winter (10/4/06–12/21/06). The early winter composite results include the week in November (11/5/06–11/14/06) which was visibly darker and analyzed separately. Short breaks in the continuous sampling occurred from 7/20/06–7/27/06 because of relocation of the sampler, and from 11/5/06–12/5/06 due to pump failure.

Elemental carbon (EC) and organic carbon (OC) concentrations were only available for the 'early summer' composite. Filter sample collection of 25 mm quartz fiber filters was done in parallel to the hi-volume filter samples; those methods and results are detailed in Hagler et al. (2007). OC and EC concentrations were obtained from this parallel sampling and used in the source apportionment analysis.

2.3. Black carbon data

Black carbon data was collected with an aethalometer (Magee Scientific Inc.) at 5 min intervals with a sample intake volume of approximately 4 lpm. After collection the data was processed using meteorological data to remove periods of camp influence to parallel the treatment of the high-volume filters. In addition, extreme outliers (>5000 ng m⁻³ or <-5000 ng m⁻³, less than 0.1% of the data) and the 30 min of data directly following filter changes were removed. As mentioned previously, approximately 20% of sampling time is lost due to sector control. It is unlikely that any significant pollution episodes were missed due to sector control as the loss of collection time is sporadic and episodes tend to last 24 h or longer. The processed aethalometer data is presented in Fig. 1 as 24 h averages.

2.4. Chemical mass balance

Chemical mass balance (CMB) analysis was conducted using the EPA CMB model, version 8.2. This receptor based model yields an effective variance, least-squares solution to the linear sum of products of source profile abundances and source contributions (Watson et al., 1984). The species included in the source apportionment analysis were EC, C₂₉ to C₃₃ *n*-alkanes, levoglucosan, 17β(H)-21α(H)-30-Norhopane, and 17α(H)-21β(H)-Hopane. Measurement uncertainty was estimated by the standard deviation of the blanks as well as the spike compound recovery values, down to a threshold uncertainty of 0.9 pg m⁻³ for *n*-alkanes, and 0.02 pg m⁻³ for hopanes. The source profiles included were vegetative detritus (Rogge et al., 1993), biomass burning (Iinuma et al., 2007), and mobile sources (Fraser et al., 1998). Fitting statistics such as *r*² (coefficient of determination), χ² (chi squared statistic), and a calculated to measured ratio for the species included in the model determine the accuracy of the resulting source contribution. Uncertainties associated with the apportioned sources are also calculated by the model. While this model is most typically used in urban areas, the general source profiles and ambient data input in this case were tailored to provide results relevant to such a remote location.

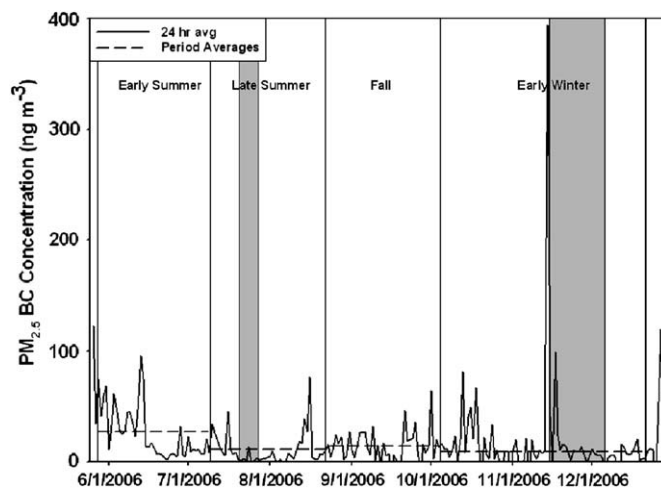


Fig. 1. PM_{2.5} aethalometer black carbon concentrations. Labeled time periods (early summer, late summer, fall, early winter) are separated by solid vertical lines and represent hi-vol filter composites. Shaded areas represent time during which hi-vol filters were not collected. The horizontal dashed lines are period averages for the BC concentrations corresponding to the hi-vol filter composites, with the omission of any measurements during the time periods that have been shaded.

3. Results and discussion

3.1. Black carbon

The black carbon (BC) data is presented in Fig. 1 as 24 h averages from the processed 5 min data. BC concentrations ranged from below detection to 340 ng m^{-3} , with an average of 20 ng m^{-3} . Values below detection, which result from extremely low 24 h average aerosol BC concentrations and instrument noise are not meaningful and are not shown in Fig. 1. Super-imposed on the BC daily average trend are the time periods that correspond to the high-volume filter composites; dashed lines are the average BC value over the time period (Fig. 1), excluding data from the periods when the high-volume filters were not collecting, which are shaded.

The concentration range of the black carbon measured at Summit, Greenland, relative to other remote locations, falls in the middle to low range of the spectrum (Table 1). While black carbon levels are the lowest in Antarctica (Bodhaine, 1995), with an average concentration of 0.7 ng m^{-3} , this is to be expected given its location in the southern hemisphere where emissions are lower (Koch et al., 2007). The levels presented for Mace Head, Ireland, (average BC 62 ng m^{-3}) represent unpolluted marine air masses, and are therefore much lower than might be expected in a location so close to highly populated areas. For the northern hemisphere, the BC concentrations recorded at Summit tend toward the lower range. This indicates that while transport from polluted regions does occur, with only limited anthropogenic pollution emissions sources in the Arctic itself, it is likely from episodic pollution plumes transported into the polar region (Eleftheriadis et al., 2009; Law and Stohl, 2007).

To perform CMB analysis for the later composites, the EC concentrations were estimated using the BC data from the aethalometer. These were calculated based on the EC to BC ratio (0.27) during the early summer period and applied to the remaining time periods. The measured EC and OC concentrations during the early summer time period were 7.1 and 61 ng m^{-3} , respectively (Hagler et al., 2007); calculated based on the data from the measurements which overlapped those of the high-volume samples only. The estimated EC values were 3.0 , 3.8 , and 2.4 ng m^{-3} for the late summer, fall, and early winter periods, respectively. These estimates were based on the BC seasonal averages which only included data from time periods when the high-volume sampler was collecting. As the full filter was used in laboratory analysis for speciation, bulk OC concentrations are only available for the early summer period.

3.2. Speciated organic compounds

Fig. 2 presents the results from the speciated organics analysis of the high-volume filter composites. In agreement with the BC data

Table 1

A comparison of black carbon concentrations from Summit, Greenland and other remote locations.

Location	Average BC (ng m^{-3})	BC Range (ng m^{-3})
Summit, Greenland	20	<0–340
Barrow, Alaska, USA ^a	30	0.28–300
Mace Head, Ireland ^b	62	47–74
Mauna Loa, Hawaii, USA ^c	6	0.1–100
Hanimaadhoo, Maldive Islands ^d	72	<50–120
South Pole, Antarctica ^e	0.7	0.01–50

^a (Bodhaine, 1995) Data from 1988 to 1993; average estimated from graph.

^b (Derwent et al., 2001) Data from 1995 to 1998; unpolluted marine air only.

^c (Bodhaine, 1995) Data from 1990 to 1993; average estimated from graph.

^d (Corrigan et al., 2006) Data from Oct. 1 to Dec. 1, 2004, transitional period between dry and monsoon.

^e (Bodhaine, 1995) Data from 1987 to 1990; average estimated from graph.

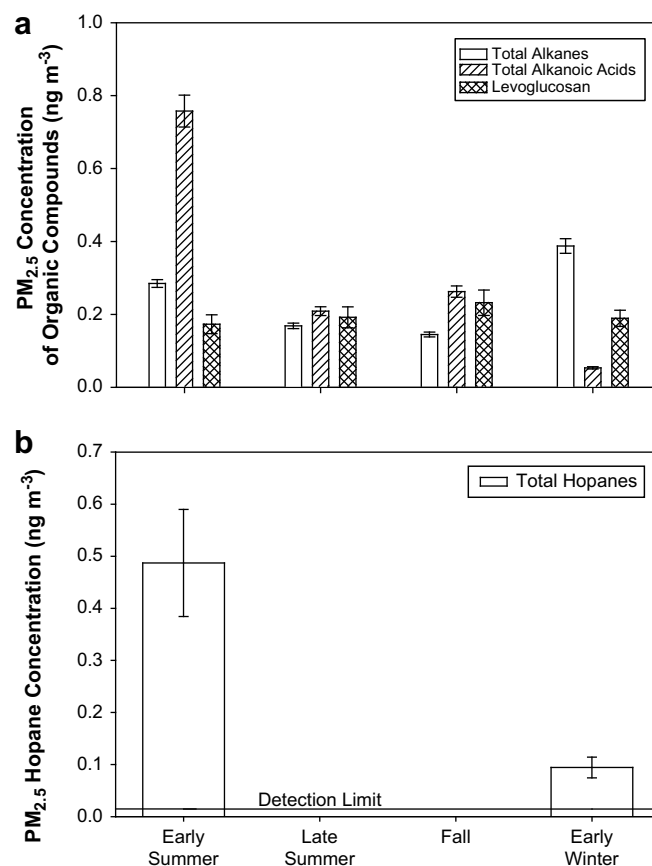


Fig. 2. PM_{2.5} concentration of (a) total *n*-alkanes, total *n*-alkanoic acids, and levoglucosan, and (b) total hopanes measured during each hi-vol composite time period.

(Fig. 1), the highest concentrations are generally observed during the early summer period. The *n*-alkanes quantified range from C₁₅ to C₃₂; these are tracer compounds which can help distinguish between biogenic and anthropogenic sources (Simoneit, 1984). The *n*-alkanoic acids quantified range from C₂₀ to C₂₉. Both are shown in more detail in Fig. 3. The hopanes quantified include 17β(H)-21α(H)-30-Norhopane and 17α(H)-21β(H)-Hopane, which are tracers for fossil fuel combustion (Schauer et al., 1996), and were not observed in the late summer or fall. Error bars are based on the standard deviation of the blanks and a percentage of the original sample concentration, which is related to spike recovery, typically ranging from 15 to 20 percent. In the case that a compound does not show up in the blanks, that portion of the uncertainty is based on the instrumental detection limit.

Hopanes are characteristic of anthropogenic origins, and more specifically of motor vehicle emissions (Rushdi et al., 2006; Schauer et al., 1996). The individual hopanes ranged from 0.06 to 0.6 pg m^{-3} (Table 2). The early summer period, and the one week that was analyzed separately had the highest concentrations of hopanes detected. In comparison to the other locations presented in Table 2, the concentrations recorded at Summit are orders of magnitude lower. This is not unexpected since Summit, Greenland is remote, and there are minimal sources of anthropogenic emissions in the surrounding region (Shindell et al., 2008; Law and Stohl, 2007).

Levoglucosan is a tracer for biomass burning, including forest fires; it can frequently be detected far from the source of emission because it has been found to be relatively stable in the atmosphere and the amount emitted from large scale fires is typically significant (Simoneit et al., 1999). The highest concentration of levoglucosan

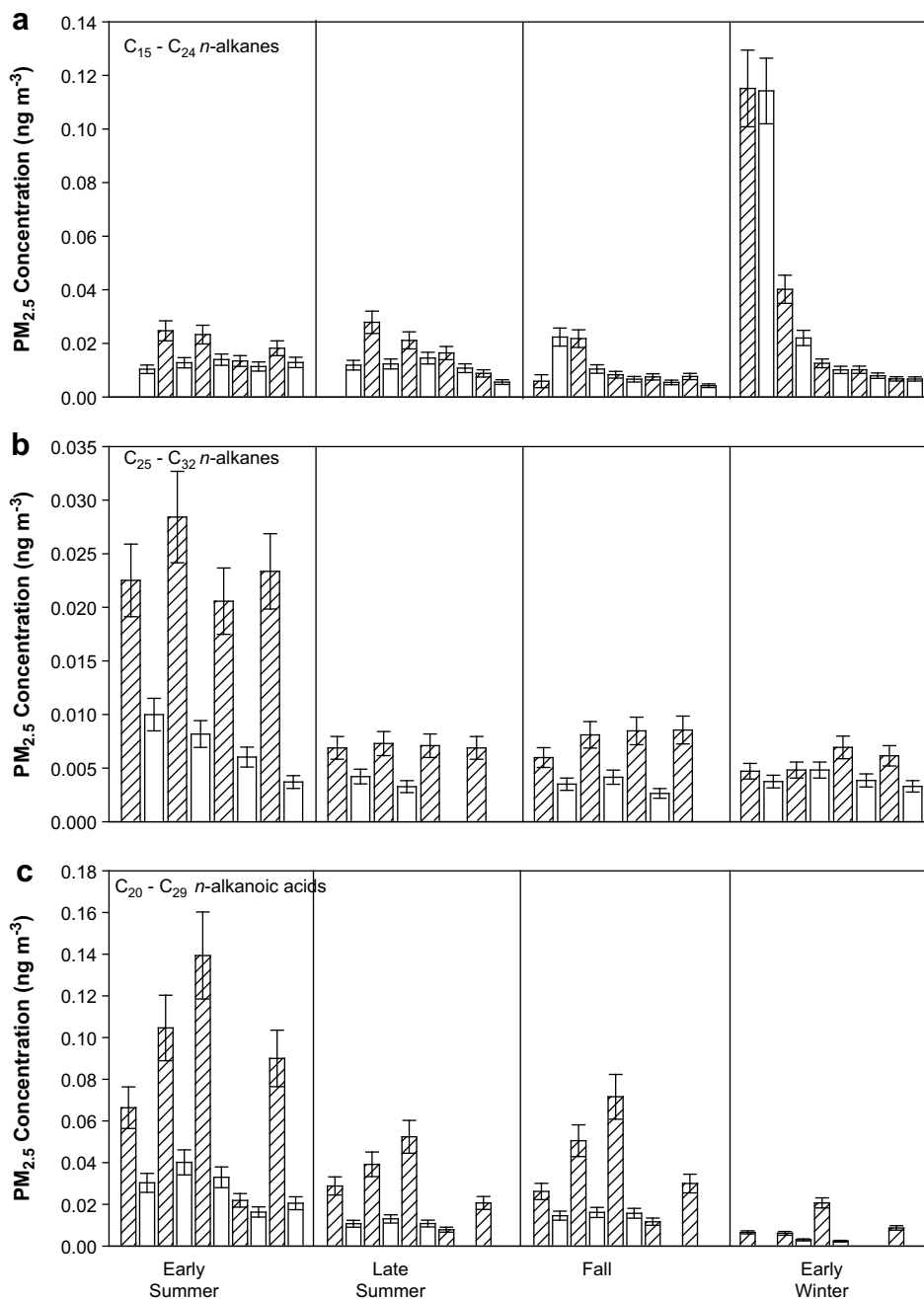


Fig. 3. Individual *n*-alkane and *n*-alkanoic acid concentrations from the PM_{2.5} aerosol at Summit, Greenland. (a) and (b) concentrations of sequential *n*-alkane homologs from C₁₅ to C₂₄, and C₂₅ to C₃₂, respectively, where odd homologs are hatched bars and even homologs are open bars. (c) concentration of sequential *n*-alkanoic acid homologs from C₂₀ to C₂₉, where even homologs are hatched and odd homologs are open bars.

was detected on the visually darkened filter that represented one week in mid-November, at 0.83 ng m⁻³. Possible changes in the source region for this episode were investigated and are available in SI. This concentration however, when incorporated in a longer time period as in the early winter period, does not represent a significant deviation from the concentrations recorded during the half-year time span, which ranged from 0.17 to 0.23 ng m⁻³. A recent paper by Stohl (2006) documented the transport of air masses into the Arctic troposphere with a focus on pollution transport of BC, including anthropogenic and forest fire emissions. Those results indicate that the source of levoglucosan at Summit could originate from forest fires in the sub-Arctic, in areas such as Alaska, northern

Canada, and the boreal forests of Siberia in Asia (Stohl, 2006), or from agricultural fires in Eastern Europe, such as those that occurred in the spring of 2006 (Stohl et al., 2007). Such large fires commonly lead to large smoke plumes that can be observed by satellite during long distance transport (Iziomon et al., 2006; Law and Stohl, 2007), and detected in places like Greenland as significant spikes, or periods of elevated concentrations of tracers such as levoglucosan (Stohl et al., 2007). During the agricultural fires in the spring of 2006, a PM_{2.5} high-volume sampler was operated on Spitsbergen in the Arctic Circle east of Greenland, from which the levoglucosan concentration in the aerosol was measured. These concentrations ranged from just above zero to approximately

Table 2

Comparison of concentrations from other locations around the world to data from this study, Summit, Greenland. Mean concentrations listed, minimum to maximum concentrations in parentheses.

Location	Levoglucosan (ng m ⁻³)	Norhopane (ng m ⁻³)	Hopane (ng m ⁻³)	Alkanes – C18; C19 (ng m ⁻³)	Alkanes – C30; C31 (ng m ⁻³)
Summit, Greenland	0.32 (0.17–0.83)	0.0004 (0.00009–0.0006)	0.0003 (0.00006–0.0004)	0.016 (0.010–0.022); 0.015 (0.008–0.023)	0.004 (0.003–0.006); 0.011 (0.006–0.023)
Maldives ^a	5.55 (1.97–8.62)	<0.25	<0.25	n.r.	n.r.
Kern Wildlife Refuge, CA ^b	22.5–25.3	n.r.	n.r.	4.90–4.96; 0.238–0.342	n.r.
Seney, MI, USA ^c	1.64 (0.46–2.81)	0.12–0.44	0.11–0.35	n.r.	1.13 (0.53–3.09); 1.63 (0.28–4.56)
Mexico City, Mexico ^d	112.9 (43.9–273.7)	0.22 (0.15–0.30)	0.15 (0.09–0.23)	n.r.	1.79 (0.89–3.06); 3.77 (1.89–8.22)

n.r. = not reported.

^a (Stone et al., 2007) Data from Hanimadoo, sampling period August 20, 2004–January 21, 2005; PM_{2.5}.

^b (Schauer and Cass, 2000) Value from two measurement periods, December 26–28, 1995 and January 4–5, 1996.

^c (Sheesley et al., 2004) Values from monthly averages from November 2001 through December 2002; if just a range is listed (as for the hopanes) the compound was detected 3 times or less throughout the sampling period.

^d (Stone et al., 2008) Milagro campaign, urban site data.

3.3 ng m⁻³ for 48–72 h filter samples that were collected from April 24 to May 10 (Stohl et al., 2007), not all that different in concentration to the concentrations measured at Summit over a much longer period of time. In July of 2004, the impact of forest fire plumes was observed at various monitoring stations in the Arctic (Stohl et al., 2006). At the same Spitsbergen monitoring station as mentioned previously, 48–72 h PM_{2.5} high-volume filter samples analyzed for levoglucosan showed concentrations ranging from <0.1 to approximately 0.25 ng m⁻³ (Stohl et al., 2006). These were lower than those recorded during the agricultural fire episode, but still indicative of a biomass burning influence and very similar to the concentrations measured in this study.

3.3. Carbon preference index

The concentration of the individual *n*-alkanes and *n*-alkanoic acids is shown in Fig. 3. Shading emphasizes any carbon preference, which can be an indicator for a biogenic or vegetative source, if for *n*-alkanes the odd predominate or for *n*-alkanoic acids the even predominate (Simoneit, 1984). The carbon preference index (CPI) was calculated for the largest set of consecutive alkanes (sum odd alkanes/sum even alkanes) and alkanic acids (sum even alkanic acids/sum odd alkanic acids) for all composite periods. All CPI values are shown in Table 3. For the alkanes, the CPI (C₁₆–C₂₉) ranged from 0.51 to 1.9, with the values decreasing over time from early summer to early winter. A CPI value of 1 (no preference) indicates an anthropogenic origin, values greater than 1 indicate biogenic origin. The amount of consecutive alkanes varied to include a larger number of alkanes depending on filter composite, however, the CPI range did not change significantly (0.5–2.0). When considering homologs C₂₅ and larger, those believed to originate mostly from plant waxes (Simoneit and Mazurek, 1982), the CPI values increased (1.4–3.4), indicating a definite influence of vegetative detritus. This influence is largest in the early summer and decreases, reaching a minimum in the early winter, as would be expected corresponding to the seasonality of vegetation in the northern hemisphere. The increasing dominance of a fossil fuel source corresponds with the decreasing influence of the vegetative

Table 3

Carbon preference index values for the different seasons.

	Early Summer	Late Summer	Fall	Early Winter
Alkanes				
C ₁₆ –C ₂₉	1.9	1.5	1.2	0.51
≥C ₂₅	3.4	1.9	2.2	1.4
Alkanic acids				
C ₂₂ –C ₂₅	3.3	3.9	3.8	5.1

source. This is supported by the increasing amount of pristane sequentially in the samples, which along with phytane has been documented to be an indicator of petroleum origin (Simoneit, 1985; Simoneit and Mazurek, 1982). Pristane and phytane concentrations ranged from 0.027 to 0.33 ng m⁻³ and 0.005–0.017 ng m⁻³, respectively. Both compounds peaked during the early winter period where the *n*-alkane CPI values indicate fossil fuels as the dominating influence. Smoke aerosol from a timber fire has also been documented to have alkanes with CPI values in the range 1.2–5 (Simoneit, 1985), yielding forest fires a likely influence, supported by forest fires documented to impact aerosol concentrations in the Arctic during the summer and fall seasons (Hsu et al., 1999; Iziomon et al., 2006; Law and Stohl, 2007; Stohl et al., 2006). Overall, these CPI values indicate likely sources of the alkanes to be of fossil fuel origin or possibly forest fire smoke aerosols as the dominating influence (Simoneit, 1984), with a vegetative detritus influence most present during the early summer period. This is supported by previous work of Grannas et al. (2004) which documented evidence of vascular plant organic matter in polar snow, citing long-range atmospheric transport of biogenic material as the source of the vascular tissue found at Summit and Alert.

The alkanic acids had a much smaller block of consecutive homologs from C₂₂ to C₂₅ across all composites, due to the limited amount of alkanic acids detected in the early winter. The CPI for this range of alkanic acids is 3.3 to 5.1, and when considering the largest consecutive block of alkanic acids for individual filter composites, ranges from 3.1 to 5.1, also not a significant variation. These results would support those from the alkanes which suggest motor vehicle exhaust or smoke aerosol sources as the dominating influence (Simoneit, 1985), with a possible smaller vegetative source. Fatty acids originating from plant waxes tend to have maxima at C₂₆, C₂₈, or C₃₀ (Simoneit and Mazurek, 1982); the acids presented here peak at C₂₄ during each period and tend to fall off in concentration following the C₂₄ peak. However, the C₂₈ fatty acid was detected in all of the composite periods at a higher concentration relative to the odd homologues. Overall, the CPI values indicate that while sources such as the vehicle exhaust or smoke aerosol likely dominate, a vegetative source is likely present as well, but contributes to a lesser degree.

3.4. Source attribution

The EPA chemical mass balance receptor model was used to estimate the relative strength of each source contribution for the organic carbon present in the PM_{2.5} aerosol from Summit, Greenland. Given the remote location of the sampling site and the lack of any significant emissions sources in the surrounding area (Law and Stohl, 2007) general source emissions profiles were used.

Fig. 4 depicts the results from the CMB analysis. These are the first source apportionment results published for the polar free troposphere, to the author's knowledge. The early summer composite is the only composite for which a complete mass balance was possible because of the parallel OC and EC measurements by Hagler et al. (2007); 4% of OC was apportioned. The EC was estimated from the real-time BC for the remaining composites to allow for the CMB analysis. The lack of OC measurements for all composites except for the early summer period does not allow for a calculation of percent of OC apportioned. However, source contributions in terms of $\mu\text{g carbon m}^{-3}$ are still calculated based on the tracer compound concentrations and source profiles. During all time periods biomass burning was an important source ($0.6\text{--}0.9 \text{ ng m}^{-3}$), while vegetative detritus ($0.3\text{--}0.9 \text{ ng m}^{-3}$) dominated in early summer and was less substantial in the remaining time periods.

The r^2 values (0.72–0.88) for the CMB results indicated good agreement between measured species and source profiles; χ^2 values (2.53–5.55) correlating the uncertainty between the measured species and sources profiles were reasonable. Further discussion on these and additional statistics is available in the SI.

The lack of hopanes (concentration less than 0.015 pg m^{-3}) during the late summer and fall composites did not allow for the inclusion of the fossil fuel source during these time periods. While the source profile is a general profile from mobile sources in North America, including different types of gasoline and diesel vehicles (Fraser et al., 1998), the source is representative of a general fossil fuel source in the case of Greenland and may include ship traffic from the surrounding oceans which have been shown to be a possible influence in the region (Law and Stohl, 2007; Xie et al., 2007). The concentration of the fossil fuel source during the early summer and early winter time periods was 0.8 ± 0.1 and $0.1 \pm 0.03 \text{ ng C m}^{-3}$, respectively.

The vegetative detritus profile is from the fine ($2.0 \mu\text{m}$) particulate matter abrasion products of green and dead leaves (Rogge et al., 1993). The vegetative detritus source contribution is the largest in the early summer ($0.9 \pm 0.1 \text{ ng C m}^{-3}$), contributing 1.5% to the measured OC, with a lesser influence over the remaining seasons, in agreement with the CPI results for the *n*-alkanes, and the seasonal patterns of vegetation in the northern hemisphere, as discussed previously. The late summer, fall, and early winter periods have concentrations of 0.3 ± 0.04 , 0.3 ± 0.05 , and

$0.3 \pm 0.04 \text{ ng C m}^{-3}$, respectively. While the source apportionment of the vegetative detritus source may seem more significant than the influence as determined by the CPI values, the *n*-alkanes make up only a small portion of the organic carbon.

The biomass burning profile is a European conifer species (pine) that was burned with green needles, as would be the case in forest fire conditions (Iinuma et al., 2007). The biomass burning source in Greenland likely originates from boreal forest fires, which have been shown to significantly impact aerosol concentrations in the Arctic (Hsu et al., 1999; Law and Stohl, 2007; Stohl et al., 2006), which is supported here by the contribution of the biomass burning source to the OC during each time period. During early summer the biomass burning contribution was $0.6 \pm 0.2 \text{ ng C m}^{-3}$, or 1.0% of the measured OC. Contributions during the late summer, fall, and early winter periods were 0.7 ± 0.2 , 0.9 ± 0.2 , and $0.7 \pm 0.2 \text{ ng C m}^{-3}$, respectively. Forest fires in the northern latitudes are likely the dominant source, however, large agricultural fires, as were documented in the spring of 2006 (Stohl et al., 2007), are also a possible, likely more sporadic, source.

The large amount of unapportioned OC during the early summer period may be indicative of a significant amount of secondary organic aerosol (SOA) present in the atmosphere at Summit. Recent studies have documented that the snowpack at Summit is highly photochemically active, affecting the atmosphere above the snowpack (Grannas et al., 2007, and references therein). Previously, unapportioned OC was attributed to SOA, especially in remote locations where long range transport and atmospheric processing, specifically the influence of photochemistry during summer months, have a large influence (Sheesley et al., 2004), as would be the case at Summit. Additionally, the water soluble portion of OC has been shown to correlate well with the amount of SOA present (Stone et al., 2008). In the case that the unapportioned OC is likely comprised mostly of SOA, it should be similar to the mass concentration of the water soluble fraction of OC. However, 71% of organic carbon from biomass burning aerosol was found to be water soluble (Sannigrahi et al., 2006), and this must be taken into account. On average 93% of organic carbon was found to be water soluble at Summit (Hagler et al., 2007); this results in $0.057 \mu\text{g C m}^{-3}$ of total OC to be water soluble. This compares very well to the amount of OC from the sum of the unapportioned fraction of OC plus the percent of water soluble OC apportioned to biomass burning, $0.059 \mu\text{g C m}^{-3}$. Therefore, it is likely that a large amount of the unapportioned OC at Summit, at least for the early summer period for which measurements exist, is due to SOA.

4. Conclusions

This paper presents concentrations of individual organic compounds of $\text{PM}_{2.5}$ aerosol collected at Summit, Greenland. This type of data is useful for source apportionment analysis, however the amount of data available of this nature is limited at this time. The low aerosol loadings make analysis of this type challenging because of the necessity for low detection limits and the many precautions that must be taken to avoid any contamination. Source apportionment analysis was conducted using the EPA chemical mass balance model. This model identified three general sources, biomass burning, vegetative detritus, and a fossil fuel source, contributing 1.0, 1.5, and 1.3 percent to measured OC during the early summer period, respectively. The remaining unapportioned OC, approximately 96%, was estimated to be SOA, resulting from long range transport of pollutants and the active photochemistry occurring at Summit (Grannas et al., 2007). The sources are general because they all likely originate far from Summit (Shindell et al., 2008; Law and Stohl, 2007), and are transported to the Arctic over several days or weeks (Stohl, 2006). These are the first source

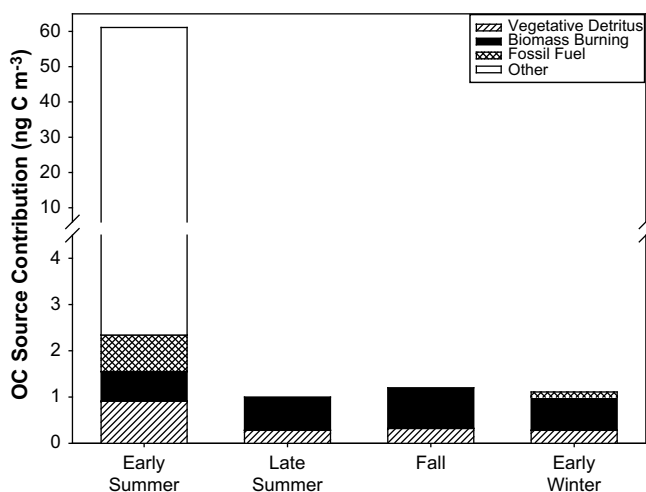


Fig. 4. Results of the chemical mass balance model depicting the source contributions of biomass burning, vegetative detritus, and a mobile source in terms of ng C m^{-3} of OC. An 'other' category is only possible for the early summer period when the concentration of OC was measured.

apportionment results for the polar free troposphere to the author's knowledge, and show that a variety of sources impact locations as remote as the Arctic. Future research in this vein, in collaboration with transport modeling studies, could be instrumental in determining not only the source, but the source region of anthropogenic pollution to the Arctic.

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2009.05.043.

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