Development and application of biomass burning tracers in ice core for reconstruction of boreal forest fire history in North America

（森林火災トレーサーの評価とアイスコアを用いた過去の北アメリカ北方林の森林火災の変遷の復元）

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Abstract:

Biomass burning, which includes wildfires and other types of fires involving plant matter, emits large amount of numerous greenhouse gases and aerosols into the atmosphere. Understanding the fire regimes, especially in boreal forest is important as, boreal forest contains one third of world's forests, and an important source of air pollutants throughout the Arctic. Hence, it is important to precisely reconstruct long-term variability of boreal fire associated with climate change for improving predictions of the impact of future climate changes on boreal fires. And for this, well-dated biomass burning tracer records are needed to study the link of climatic with boreal forest fire in the past. Forest fire activity in a past could be reconstructed by analyses of biomass burning tracers (levoglucosan and dehydroabietic acids) in paleoclimate archives such as ice core. Levoglucosan is a marker of biomass burning and dehydroabietic acid is a specific tracer of conifer tree burning. In recent years, these tracers have been applied to few ice cores to reconstruct the variability of such aerosol loadings in the past. However, paleoclimatic utility of these tracers in ice core has not been evaluated well.

Thus, we assess the paleoclimatic utility of the biomass burning tracers in Greenland ice core (SE-Dome ice core). Comparison of biomass burning tracers in the SE-Dome ice core with area burned events in a possible source region of biomass burning aerosol suggests that the ice core tracer records document most of the pronounced biomass burning events in eastern Canada. This confirms that analyses of the biomass burning tracers in Greenland ice cores are promising approach to reconstruct the frequency of significant biomass burning events in regional scale.

Next, we applied the two tracers to ice cores collected from northwestern Greenland (Sigma D) and southern Alaska (Aurora peak) to reconstruct the boreal forest fire history in North America over the past few hundred years. The both ice core records indicate that significant boreal forest fire events happened frequently in Alaska and Canada over the past 300 years with increases in boreal fires during Little Ice Age and the recent decades. Comparison of regional temperature and ice core biomass burning tracer records indicates that regional temperature is the major driver intensifying the fire in Canada and Alaska on decadal timescales, as prominent peaks of biomass burning tracers well correspond to the regional climate warming periods. In addition, changes in the decadal scale climate oscillations such as North Atlantic Oscillation (NAO), likely exert an influence on fire dynamics in eastern Canada, by increasing aridity. On the other hand, strong link between decadal scale climate oscillations and boreal fire is not recognized in the western boreal region over the past 300 years. The coupling of boreal fire and regional temperature for the last 300 years, suggest that occurrence frequency of boreal forest fire will increase in a future due to the ongoing global warming.

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Abbreviations

BB	Biomass burning
LG	Levoglucosan
DA	Dehydroabietic acid
VA	Vanillic acid
BC	Black carbon
BrC	Brown Carbon
BVOC	Biogenic volatile organic carbon
3-HGA	3-hydroxyglutaric acid
2-MT	2-methyl tetrol
2-MG	2-methylglyceric acid
LIA	Little ice age
AO	Arctic oscillation
AMO	Atlantic multi decadal oscillation
NAO	North Atlantic oscillation
PDO	Pacific decadal oscillation

Chapter 1

Introduction

This chapter provides a brief introduction of the effect of biomass burning on climate with special emphasis on the biomass burning aerosols from boreal forest fire and the importance of reconstruction of the past forest fire history. Here, it has been discussed that, how the biomass burning product emitted and long range transported to glacier ice. A brief discussion about all types of fire proxies have also been given here. Furthermore, this chapter also includes the gap in the previous research works and purpose of my thesis.

1.1. Effect of biomass burning on climate

Biomass burning (BB) is considered as a significant air pollution source, as it emits large amount of numerous greenhouse gases and aerosols into the atmosphere such as CO_2, CO, CH_4, black carbon (BC), brown carbon (BrC), alcohols, organic acids, and persistent organic pollutants (Andreae and Merlet, 2001; Crutzen et al., 1979; Lamarque et al., 2010; Mukai and Ambe, 1986). BB is ubiquitous (Fig. 1.1) and play an important role in climate warming by emitting 1/5 of the CO_2 and other greenhouse gases (Jacobson, 2014; Langenfelds et al., 2002). On the other hand, BB derived aerosols also significantly influence climate by scattering and absorbing the radiation or acting as cloud condensation nuclei (Aalto et al., 2001; Haywood and Ramaswamy, 1998; Jacobson, 2001). Although BB intensity is relatively lower in northern high latitudes compared to mid-latitude countries (Fig. 1.1), global warming is predicted to occur mostly in northern high latitude（Hansen et al., 2010）.

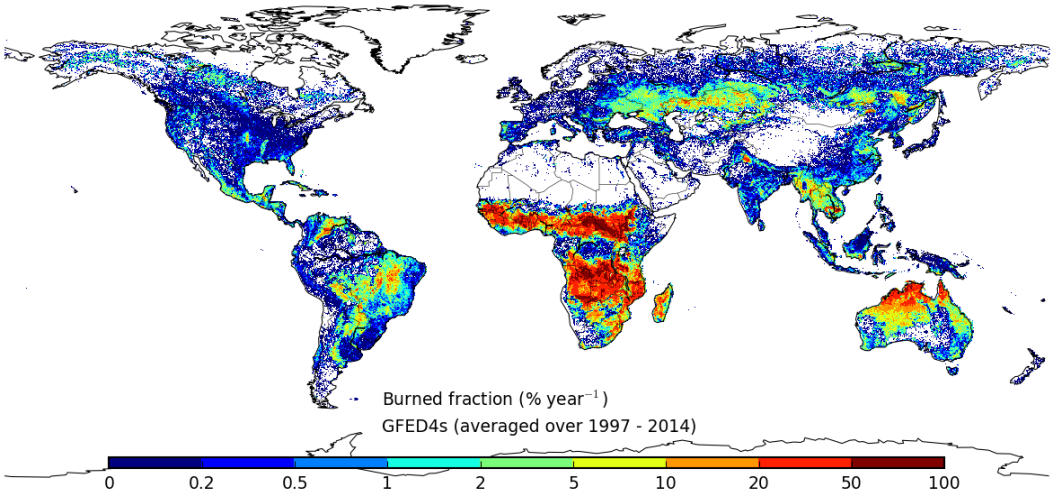

Figure 1.1: Global map of annual burned area (as percentage of the area of the grid cell), averaged over 1997-2014 (http://www.globalfiredata.org/index.html).

1.2. Radiative impact of biomass burning aerosols

BB aerosol consists of two major chemical components: black carbon (BC), which primarily absorbs solar radiation, and organic matter (OM), which scatters as well as absorb solar radiation. The absorbing component of OM is referred to as brown carbon (BrC). The presence of BC aerosols results in the absorption of solar radiation, which reduces the solar radiation reaching the Earth's surface. At the same time, these aerosols absorb the upward solar radiation reflected from below and reduce the solar radiation reflected to space. On the other hand, the absorption of solar radiation by BrC increases towards the shorter wavelengths from visible to UV (Alexander et al., 2008). Therefore, the effect of BC and BrC aerosols opposes the cooling effect of other aerosols at the top of the atmosphere. The changes arising from the aerosol scattering and absorption of solar radiation are referred to as their direct radiative forcing. Aerosols can also modify the solar radiation through their role in cloud condensation and as ice nuclei, an effect known as aerosol indirect radiative forcing (Fu, 2015).

Chung et al., (2012), estimated that the mean aerosol (OM+BC+BrC) direct radiative forcing is globally positive (Fig. 1.2). Further, Walter et al. (2016) and Lisok et al. (2018) studied the radiative impact of the BB aerosols in the atmosphere of Canada and Alaska. The BB aerosols in the soot layer absorbs the incoming radiation, leading to a local warming. Conversely, less radiation is able to reach the lower levels near the ground, which leads to a temperature reduction in comparison with a smoke-free atmosphere. Temperature changes in various atmospheric layers affect the atmospheric stratification (Walter et al., 2016). Lisok et al., (2018) found that the mean radiative forcing in the BB plume is actually positive and, the heating rate inside the biomass-

burning plume is estimated to be 1.8 $Kday^{-1}$ in the atmosphere of Northern Hemisphere. However, LIU and LIAO, (2017) estimated aerosol effective radiative forcing and surface temperature in the atmosphere of china and found that mean aerosol radiative forcing is negative and surface temperature has decreased in last 150 years. Hence, the estimation of radiative forcing of combined BB aerosols is still have large uncertainties. And these uncertainties in understanding of these BB aerosol's effects limit our knowledge about climate change.

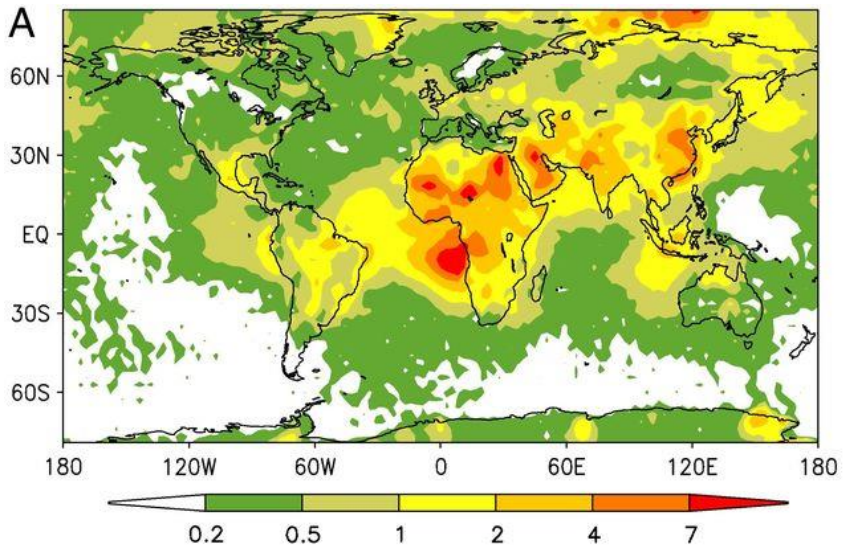

Figure 1.2: global map of annual mean aerosol (OM+BC+BrC) direct radiative forcing (Wm^{-2}) (Chung et al., 2012)

1.3. Importance of biomass burning in boreal region

Although BB occurs in all over the world, the BB in the boreal regions have special impact on the climate. The circumpolar boreal forest contains one third of world's forests (Fig. 1.3a), with half of the world forest carbon (Conard et al., 2002) and

and an important source of air pollutants throughout the Arctic (Lavoué et al., 2000; Quinn et al., 2008). Additionally, another reason for concerning about BB in the boreal reason is boreal forests are at the lattitide, where most of global warming are predicted to occur (Fig. 1.3b) (Hansen et al., 2010). Hence, if the frequency of boreal fire will increase, it may lead to increase of emission of many pollutant in the atmosphere, which led to accentuate the warming in the Northern lattitude. For this purpose, it is necessary precisely reconstruct long-term variability of BB and its emission from boreal forest fire, to understand how fire regimes have changed in the past, which in turn may provide insight into how climate changes and human densification may influence fire.

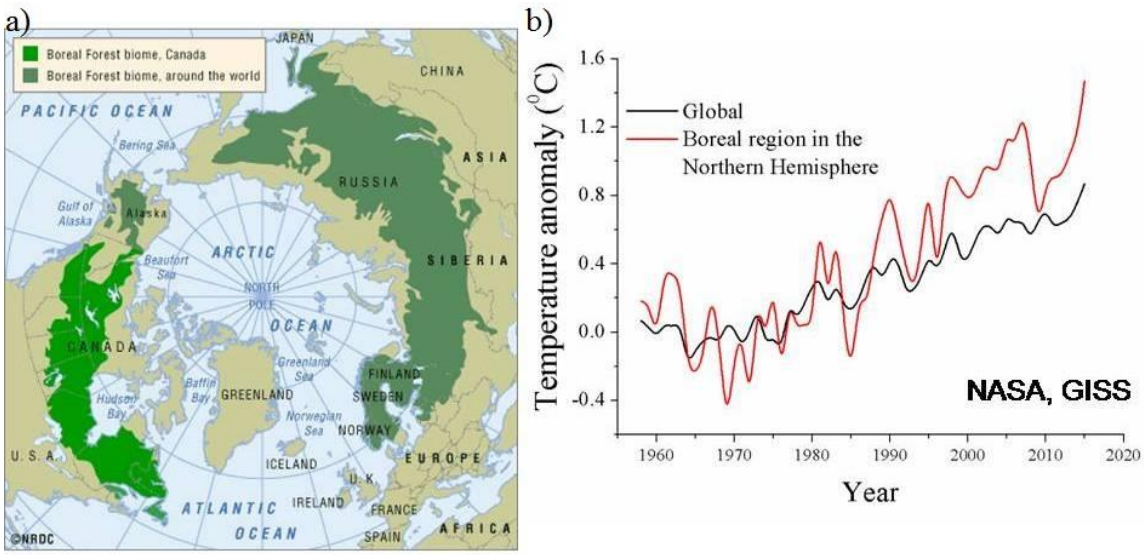

Figure 1.3: a) Map showing the boreal regions (green color) in the Northern hemisphere (cite reference!) b) Comparison of last 60 years temperature anomaly in global scale and in the boreal regions (cite reference!).

1.4. Paleoclimate archives:

When BB held in a forest, BB products are emitted to the atmosphere and are transported to the adjacent and remote regions and are finally deposited in paleoclimate archives such as marine and lacustrine sediment as well as glacier and ice sheet (Fig. 1.4). Thus numerous chemical species emitted or produced from BB are trapped in ice (Legrand and Mayewski, 1997) and sediment (Hodell et al., 1999) archives. A diverse range of paleo-proxies has been proposed to reconstruct BB, including fire scars on tree rings, sedimentary charcoal records, and ice core records of gases and aerosol-borne chemicals (Hodell et al., 1999; Jones and Mann, 2004). Since ice core preserves key climate factors that influence radiative balance in the atmosphere such as greenhouse gases and atmospheric aerosols and also can record regional scale climatic history (Kawamura et al., 2012; Legrand et al., 2013; Legrand and Mayewski, 1997; Lüthi et al., 2008; Petit et al., 1999; Preunkert and Legrand, 2013; Zennaro et al., 2014), ice core is often considered as a special archive among the different paleoclimate archives. Several factors (i.e. BB magnitude, wind regime, snow accumulation rate) may affect the concentrations of the BB product in glacial ice. For a BB signal to be recorded in glacial ice, meteorological conditions and transport distances must be favorable for transport of the aerosol plume from the forest fire site to ice core site (Whitlow et al., 1994). However, primary factor, which control the concentrations of the BB products in ice core, still remains uncertain.

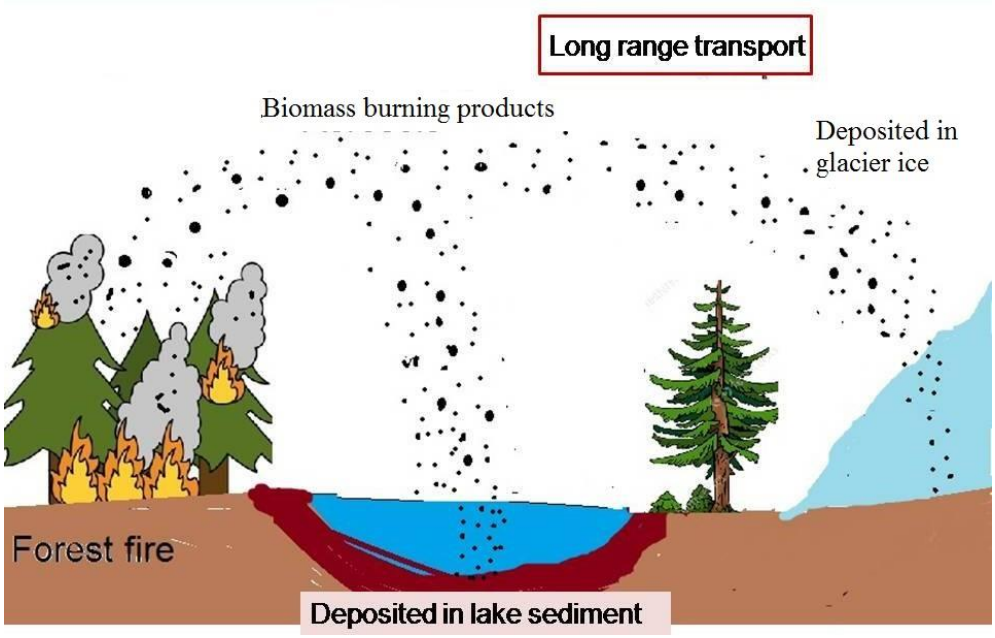

Figure 1.4: Emission of BB aerosols and tracers and deposition in lake sediment and glacier ice.

1.5. Conventional biomass burning tracers

Proxy records of BB are important for understanding the relationship between climate and fire variabilities over long timescales. Many studies attempted to reconstruct the past BB history in different regions based on a number of proxies (black carbon, potassium, ammonium, formate, charcoal, isotopic composition of trace gases) (Anderson et al., 2006; Eichler et al., 2011; Grieman et al., 2017; Hicks and Isaksson, 2006; Kawamura et al., 2012; Olivier et al., 2003; Whitlow et al., 1994; Yalcin et al., 2006; Zennaro et al., 2014). However, using the inorganic tracers and isotopes to reconstruct past BB history, have some limitations, as they have multiple sources along with plant burning (Rubino et al., 2016). The sources of those conventional BB tracers

are given in table 1.1. Because of those multiple sources, interpreting the fire signals using these conventional tracers in ice core may not deliver the proper fire history.

Table 1.1: Conventional BB tracers with multiple potential sources, which are found in ice core.

Tracers	**Sources along with biomass burning**	**References**
Ammonia	Biomass burning (smoldering fires), emissions from vegetation and soil microbial activity	(Eichler et al., 2009; Legrand et al., 1992; Taylor et al., 1996)
Black carbon	flaming combustion of plants and combustion of fossil fuel	(IPCC, 2013a; Rubino et al., 2016)
Potassium	Biomass burning, sea salt, mineral aerosol	(Laj et al., 1997)
Oxalate	Biomass burning and vehicular emission	(Kawamura and Kaplan, 1987)
Carbon isotope ratios in methane	Indication of biomass burning and wetland emissions	(Fischer et al., 2008; Fisher et al., 2011)

1.6. Organic biomass burning aerosol tracers

Compared to those conventional BB tracers, using organic aerosol tracers (i.e., levoglucosan and dehydroabietic acid, vanillic acid and p-hydroxybenzoic acid) are advantageous, as they are solely produced from plant burning (Fig. 1.5) (Nolte et al., 2001; Simoneit et al., 1999). Regional fire history could be reconstructed by their analyses in ice core (Grieman et al., 2016; Parvin et al., 2019; Zennaro et al., 2014). Levoglucosan (LG) (1,6-anhydro-b-D-glucopyanose) is emitted from the thermal breakdown of cellulose and hemicellulose during high temperature (>300℃) combustion and is relatively stable in the atmosphere (Fraser and Lakshmanan, 2000). The emission of BC from BB can also be inferred by quantifying the LG abundances

(Yttri et al., 2014). on the other hand, dehydroabietic acid （DA) is a resin acid, which is emitted into the atmosphere during the combustion of softwood (coniferous wood) (Simoneit, 2002; Simoneit et al., 1999), can be use as a tracer of conifer tree burning (Simoneit & Elias, 2001). Unlike LG, which can be used to trace all kinds of plant combustion, DA is found mainly in plumes from burning of softwood conifer trees and therefore can be used to distinguish softwood from hardwood combustion (Fine et al., 2002a, 2002b).

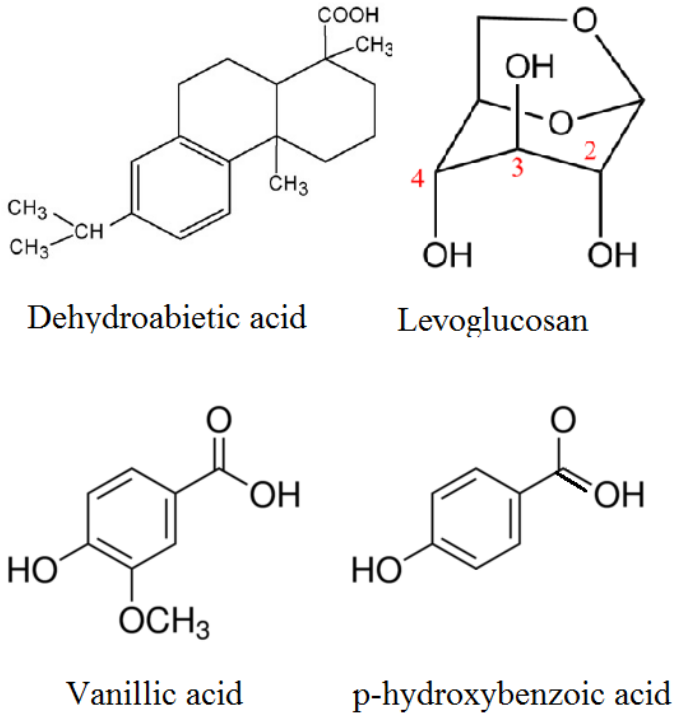

Figure 1.5: Chemical structure of the organic biomass burning tracers

Wildfire also generates phenolic breakdown products that are derived from the pyrolysis of lignin during the smoldering stage of a fire (Akagi et al., 2011; Legrand et al., 2016; Simoneit, 2002). The chemistry of these emissions reflects the composition of

the precursor lignin, the rate, temperature and oxidative conditions under which burning occurs. Aromatic acids, such as vanillic acid, para-hydroxybenzoic acid are molecules that are also tracer of BB, because they retain the basic aromatic building block of the precursor lignin (Simoneit et al., 2000, 1999). laboratory studies have shown that vanillic acid (VA) produces from the burning of North American and European conifer and deciduous tree species, while North American tundra grass fires produce para-hydroxybenzoic acid (Nolte et al., 2001; Oros and Simoneit, 2000; Simoneit, 2002). However, among these organic BB tracers, productions of LG and DA are more abundant compared to VA, para-hydroxybenzoic acid in aerosol and ice core (Haque et al., 2016; Kawamura et al., 2012). Hence, utilizing LG and DA for interpreting fire history are more advantageous as they are found in relatively higher concentrations.

1.7. Secondary organic aerosols in the atmosphere and their impact on climate

Along with BB, organic aerosols are also emitted from many other sources in land and ocean such as soil, organisms and sea spray (Carslaw et al., 2010). Organic aerosols are emitted from anthropogenic and natural sources via primary emission and secondary photochemical oxidation of various precursors into the atmosphere (Guenther et al., 2006; Kunwar B, 2014). Vegetation (trees, shrubs and grass) emits biogenic volatile organic carbon (BVOC) into the atmosphere constitutively or in response to a variety of stimuli (Holopainen and Gershenzon, 2010). These BVOC emissions undergo rapid oxidation in the atmosphere, generating the climate pollutants such as ozone and biogenic secondary organic aerosol (BSOA) (Adams et al., 2000; Arneth et al., 2009). Moreover, the BVOCs have their primary sink in the troposphere through reaction with

hydroxyl (OH) radical, which is also the main sink for methane. Because of this competition for the OH sink, rising in the emissions of BVOCs had an increasing impact on lifetimes of the greenhouse gases, i.e. methane (Schurgers et al., 2009) and consequently contribute to global warming and climate change. It is believed that secondary organic aerosol (SOA) are more abundant than directly emitted primary organic aerosol (POA) and act as a climate condensation nuclei, influencing local climate and radiative forcing (Claeys et al., 2004). These secondary aerosols can be measured by tracer based approach. Among SOAs, some of the aerosols are specifically produced from the photo oxidation of isoprene or monoterpene BVOCs (Carlton et al., 2009). These aerosols act as isoprene or monoterpene derived SOA tracers. Figure 1.6 shows how the SOA and SOA tracers are produced from the photoxidation of isoprene BVOC. Isoprene tetrols and 2-methylglyceric acid formed in the atmosphere by isoprene oxidation, which are considered as tracers of isoprene derived SOA.

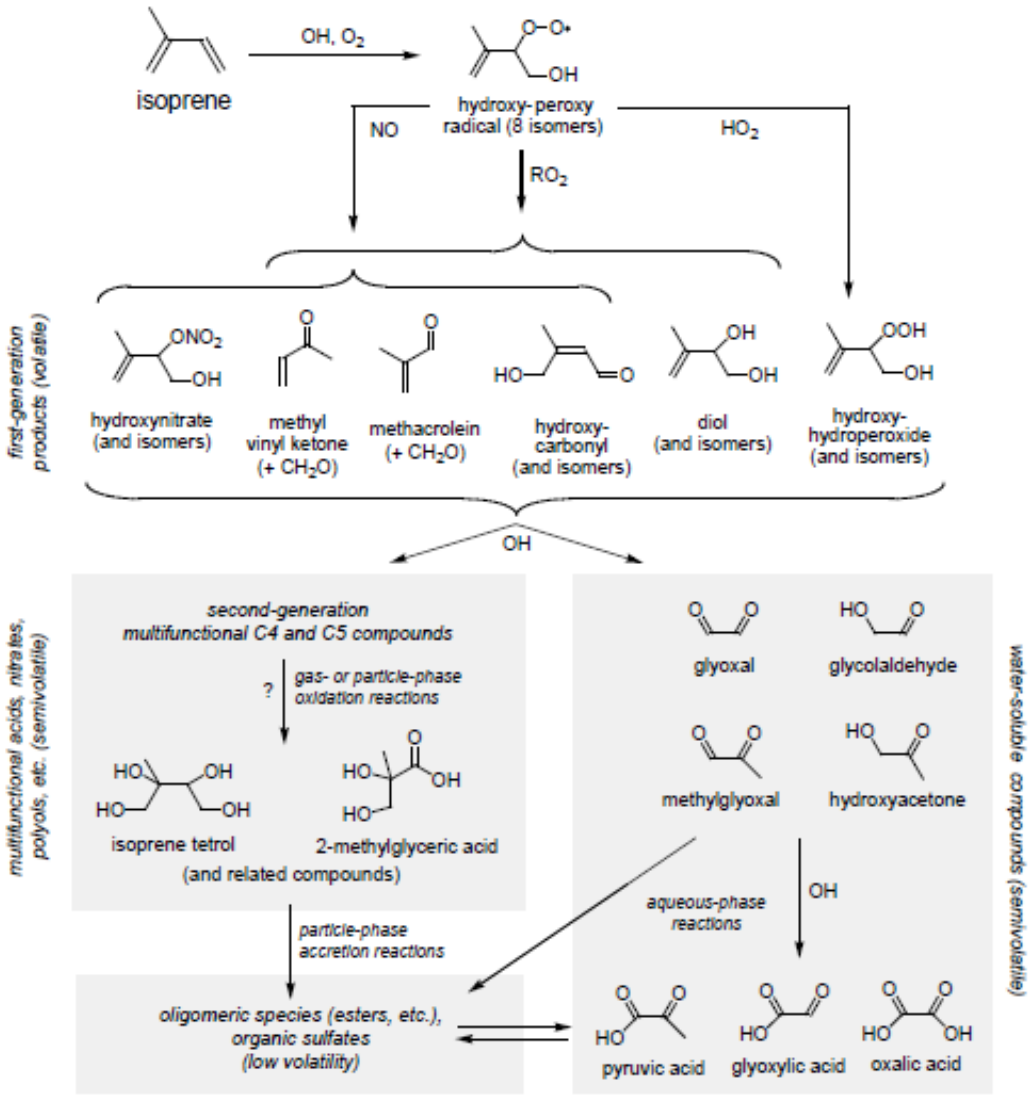

Figure 1.6: Oxidation pathways of isoprene leading to SOA formation (Carlton et al., 2009).

1.8. Purpose of this study:

It is vital to precisely reconstruct long-term variability of BB and aerosol loadings from boreal forest fire to understand the role of past climate on boreal fire and aerosol emission, which in turn will aids in the prediction and interpretation of future fire projections anticipated with climate changes. In recent years, LG have been applied to reconstruct the fluctuation of such boreal fire intensity in the past using Ushkovsky and Greenland ice core (Kawamura et al., 2012; Zennaro et al., 2015, 2014). DA has only been used by Kawamura et al. (2012) from Ushkovsky ice core. However, several factors can potentially influence the records of BB molecular tracers in ice cores. Moreover, the emission of those tracers from the source and utility of BB tracers in ice cores has not been extensively evaluated. In order to address these issues, this thesis aims to

1. assess paleoclimatic utility of LG and DA as BB proxy in ice core.
2. reconstruct boreal forest fire history in North America over the past few hundred years based on organic tracer analyses in ice core to investigate the link between climate change and fire frequency.
3. reconstruct the historical record of carbonaceous aerosol loading from Greenland ice core.

Chapter 2

Experimental Methods

The methods of the ice core BB tracer study consist of four parts, including ice core sample collection, dating of the ice cores, organic aerosol tracer and BrC analysis in the ice core and source identification of the organic aerosol tracers based on airmass backward trajectory analysis. We have generated the organic aerosol tracers data from three different ice cores and used published set of data from two other ice core sites for comparison (Fig. 2.1). The methodologies for the organic BB tracer analysis, BrC measurment and source identification are same for all the ice cores. Hence these two procedures are described in this chapter. On the other hand, sampling procedure and dating of the ice core are different among the ice core sites. Hence, these methods are discussed in chapters 3 and 4.

Figure 2.1: Geographical locations of all the ice core sites. The black dot indicates the ice core sites, which we use to generate organic aerosol tracers data. The star sign indicates the ice core sites, whose BB tracers data have already been published (Kawamura et al., 2012; Zennaro et al., 2014). We utilized these published data in our analysis.

2.1. Organic tracer analyses

2.1.1. Sample preparation

After collecting the sample of ice core and determining the ages of the cores, the ice core samples were cut into 50-cm-long pieces and were stored in a cold room (~20°C) at the Institute of low Temperature Science, Hokkaido University, until analysis. The top 5 mm of the surfaces of the ice core sample were shaved off with a

ceramic knife to remove possible contamination. Each sample was then melted in a pre-cleaned Pyrex beaker and treated with $HgCl_2$ to prevent microbial degradation of the organic compounds. Then, the samples were stored at 4°C in pre-cleaned brown glass bottles until analysis.

The samples were prepared for analysis using a method described elsewhere (Fu et al., 2008; Kawamura et al., 2012). In brief, the melt water samples were transferred to a pear-shaped flask and concentrated to nearly complete dryness using a rotary evaporator under a vacuum. The total organic matter in the dried samples was extracted with a 2:1 v/v solution of CH_2Cl_2/CH_3OH using an ultrasonic bath. The extracts were passed through a glass column packed with quartz wool and further eluted with CH_2Cl_2 and CH_3OH to extract the organics potentially adsorbed on the particles. The eluents were then combined with the extracts, transferred to 1.5-mL glass vials, and dried under a pure nitrogen gas stream. Polar organic markers in the extracts were derivatized with 99% N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) + 1% trimethylsilyl chloride for 3 h at 70°C in a sealed glass vial (1.5 mL). The derivatives were then diluted by the addition of n-hexane containing C_{13} n-alkane as an internal standard prior to the determination via gas chromatography-mass spectrometry (GC-MS).

2.1.2. Identification and quantification of the organic tracers by Gas Chromatography/Mass Spectrometry (GCMS)

GC-MS analyses were performed on a Hewlett-Packard model 6890 GC coupled to a Hewlett-Packard model 5975 MSD using a capillary column (HP-5MS, 60m×0.32mm I.D.×0.32 μm film thickness) and a split/splitless injector. The GC oven temperature

was programmed from 50°C (2 min) to 120°C at 30°C/min, then to 300°C at 5°C/min, and maintained at 305°C for 15.60 min. Helium was used as a carrier gas. Levoglucosan (LG) and Dehydroabietic acid (DA) were identified by comparing the mass spectra with those of authentic standards (Fu et al., 2016; Kawamura et al., 2012). Recoveries for the standards or surrogates were better than 80%. The analytical errors in the triplicate analyses were within 15%. A laboratory blank was measured using Milli-Q water and showed no contamination for any target compounds.

2.2. Measurements of the Light-Absorbing Properties of Brown Carbon

The light absorbing properties of BrC has been determined by the method described elsewhere (Helms et al., 2008; Yamashita et al., 2013). Glassware was cleaned with mild detergent and copiously rinsed with Milli-Q water and then either combusted at 450°C or autoclaved before use. All containers were rinsed several times with melted ice core samples before filling. The melted ice core samples were then filtered using 0.45 μm cutoff PVDF syringe filters (Millipore Millex GV, Germany). The filtered water samples were thawed and allowed to stand until reaching room temperature (approx. 23^0C) prior to absorbance measurements. Absorbance spectra were obtained between 200 and 1000 nm at 0.5 nm intervals using a spectrophotometer (UV-1800, Shimadzu). A 10 cm quartz-windowed cell was used for the absorbance analysis. Absorbance spectra of a blank (Milli-Q) and samples were obtained against air, and a blank spectrum was subtracted from each sample spectrum. Sample spectra were baseline corrected by subtracting average values ranging from 590 to 600 nm from the entire spectrum, and then converted to absorption coefficients, a(λ) (m^{-1}). The absorption coefficient at 320 nm, a(320), was reported as a quantitative parameter of

BrC (Yamashita and Tanoue, 2009). Specifications for the spectrophotometer (UV-1800) provided by the manufacture are as follows; photometric repeatability is less than ±0.001 optical density (OD) unit at an absorbance of 0.5OD and noise level is less than 0.00005. The 0.001OD corresponds to absorption coefficients of 0.023 and 0.046 (m^{-1}) for 10 cm and 5 cm measurements, respectively.

2.3. Backward-trajectory analysis

To investigate the source regions of the chemical species preserved in the ice core, air mass transport pathways were analyzed using HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) distributed by the National Oceanographic and Atmospheric Administration (Stein et al., 2015). Points at 10 m, 500 m, 1000 m, and 1500 m above ground level (a.g.l.), which correspond to 1560 m, 2050 m, 2550 m, and 3050 m a.s.l. in the model, were set as the starting points of the 10-day backward trajectories. The probability distribution of an air mass below 1500 m a.g.l. was calculated at a 1° resolution. We assumed wet deposition for the preserved aerosols and tracers (Iizuka et al., 2018). It has been reported that wet deposition produces about 90% of the BC, sulfate, and dust depositions in polar region (Breider et al., 2014). This suggests that wet deposition is also important process to eliminate water soluble organic aerosol such as LG and DA from the atmosphere. Therefore, the probability was weighted by the daily amount of precipitation when the air mass arrived at the core site. We used the daily precipitation in the reanalysis datasets of ERA-40 and ERA-Interim, both produced by ECMWF (European Centre for Medium-Range Weather Forecasts) (Dee et al., 2011; Uppala et al., 2005). To maintain consistency between the two precipitation products for the entire period (1958–2014), the daily precipitation of ERA-

40 (p40) was calibrated with that of ERA-Interim (pi) via a linear regression obtained for the period of 1979–2001 (pi = 1.36p40, R^2 = 0.862, $p < 0.001$). Based on the probability distribution, we also calculated the regional contribution, for which land regions in the Northern Hemisphere was divided into 6 regions based on national boundary.

Chapter 3

Assessment for paleoclimatic utility of biomass burning tracers in ice core

In this study, we provide continuous records of biomass burning molecular tracers (levoglucosan and dehydroabietic acid) in a Greenland ice core collected from the Southeastern Dome (the SE-Dome ice core) over the past several decades to assess the paleoclimatic utility of these tracers in Greenland ice cores. An air mass backward-trajectory analysis indicates that eastern Canada is likely the primary source region of the biomass burning tracers. Comparisons of levoglucosan and dehydroabietic acid data in the SE-Dome ice core and area burned (vegetation fire) events in Canada suggests that the biomass burning tracers in the ice core document most of the pronounced biomass burning events in eastern Canada over the past several decades, confirming that analyses of biomass burning molecular tracers in Greenland ice cores are useful to reconstruct the frequency of significant biomass burning events in regional scale. However, our study also highlights that the wind pattern when the biomass burning occurs is decisive for the registration of a biomass burning event in an ice core even though long-term changes in the wind regime associated with decadal-scale climate oscillations do not significantly influence the transport and deposition of biomass burning tracers on the Greenland ice sheet.

3. 1. Introduction

Aerosol particles emitted during burning may cause a short-term cooling of the global climate, while longer-lived greenhouse gases may cause warming after several decades (Jacobson, 2004). Therefore, the effects of BB products on the climate are complicated and their net radiative effects still contain large uncertainties (IPCC, 2013b). Therefore, to better understand the substantial impact of BB on the climate, it is important to generate long-term reliable records that document the variability of BB events.

Paleoclimate archives containing annual layers (e.g., ice cores, tree rings, sediment cores, and coral reefs) record decadal-scale climatic oscillations in the past (Hodell et al., 1999; Jones and Mann, 2004). Because ice cores preserve key climate factors that influence the radiative balance in the atmosphere, such as greenhouse gases and atmospheric aerosols (Kawamura et al., 2012; Legrand et al., 2013; Legrand and Mayewski, 1997; Lüthi et al., 2008; Petit et al., 1999; Preunkert and Legrand, 2013; Zennaro et al., 2014), ice cores are often considered to be exceptional compared to other paleoclimate archives.

A number of tracers (e.g., inorganic: potassium and ammonium, formate; organic: levoglucosan, dehydroabietic acid, and vanillic acid; and the isotopic compositions of trace gases) have been proposed to reconstruct changes in the BB activity in the past (Bock et al., 2017; Legrand et al., 2016, 1992; Rubino et al., 2016; Simoneit et al., 1999) and have been applied to ice cores (Iizuka et al., 2018; Kawamura et al., 2012; Zennaro et al., 2014). Of these tracers, organic tracers are becoming increasingly common tools because they are produced solely by BB (Simoneit et al., 1999). LG is the pyrolysis product of cellulose and hemicellulose, that are the major components of

woody part of plant, at temperatures >300°C (Andreae and Merlet, 2001), has been proposed as a general tracer of BB in atmospheric aerosols, ice cores, and sediment cores (Elias et al., 2001; Fu et al., 2012; Hu et al., 2013; Kawamura et al., 2012; Schüpbach et al., 2015; Simoneit, 2002; Simoneit et al., 2000; Zennaro et al., 2015, 2014). Conversely, DA has been proposed as a more specific tracer of the burning of conifer trees because DA is produced by the pyrolytic dehydration of abietic acid, which is a principal component of conifer resin (Simoneit, 2002; Simoneit et al., 1993). These BB tracers are injected into the atmosphere in convective smoke plumes and then are scavenged from the air column primarily by wet deposition and incorporated into firn and eventually glacial archives in the Arctic region (Gambaro et al., 2008). In recent years, these BB tracers have been applied to ice cores to reconstruct the variability of such aerosol loadings in the past (Grieman et al., 2017; Kawamura et al., 2012; Taylor et al., 1996; Zennaro et al., 2015, 2014). However, there are several factors that can potentially influence the records of BB molecular tracers in ice cores. Moreover, the emission of those tracers from the source and utility of BB tracers in ice cores has not been extensively evaluated.

To assess the paleoclimatic utility of these BB tracers in ice cores, it is vital to generate continuous records of BB aerosol tracers in ice cores with well-constrained chronologies and then compare the ice core tracer record with observationally based records of BB in the potential source region of the BB aerosol. In this study, we provide continuous records of BB aerosol tracers (LG and DA) in a well-dated Greenland ice core over the past 60 years to evaluate the reliability of the LG and DA data in ice cores as tracers of BB events.

3.2. Sampling site and age model

The ice core (90.45-m depth) was drilled in 2015 from the dome site in Southeast (SE) Greenland (67.18°N 36.37°W, 3170 m a.s.l.) (Fig. 3.1). The annual mean temperature at the SE-Dome site was−20.9°C based on a 20-m-deep firn temperature measurement (Iizuka et al., 2016). From 1958 and 2014, the SEIS2016 age scale, which is determined via the oxygen isotope matching method, was used. The SEIS2016 age scale was carefully evaluated with independent age markers, and its precision is within two months (Furukawa et al., 2017; Iizuka et al., 2018). The average accumulation rate of the SE-Dome ice core was 1.01± 0.22 m/yr, which is the highest rate of any ice core reported in Greenland. In addition, melt layers are relatively infrequent in the SE-Dome ice core. Therefore, the post depositional alteration of the deposited aerosols due to ice melt and low accumulation is thought to be minimal (Iizuka et al., 2018). This ice core is ideal to assess the paleoclimatic utility of aerosol tracers in ice cores by a precise comparison with observationally based records.

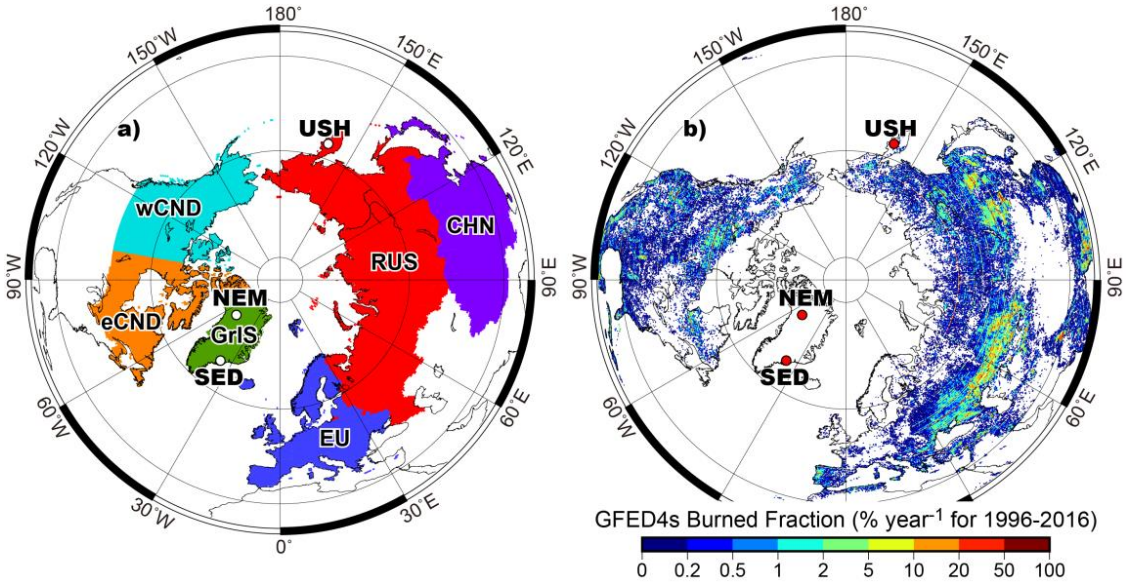

Figure 3.1. Map showing (a) the location of the SE-Dome (SED) ice core in Greenland and six regions for calculating regional contribution (GrIS: Greenland, EU: Europe, RUS: Russia, CHN: China+Japan, wCND: western Canada, eCND: eastern Canada), and (b) the percentage of the burned fraction on the globe per year (averaged over 1997–2016), (http://www.globalfiredata.org/index.html) with the locations of the SE-Dome, NEEM (NEM), and Ushkovsky (USH) ice cores.

3.3. Results and discussion

3.3.1. Source region assignment of the BB tracers via backward-trajectory analyses

First, we attempted to constrain the potential source areas of the LG and DA deposited in the SE-Dome ice core based on the probability distribution of the integrated 7-day backward-trajectory analyses during the period from 1958 to 2014 (Fig. 3.2a). According to the probability analyses, the source regions of these BB tracers are thought to be around southeastern and/or southern Greenland, the North Atlantic Ocean, and North America (more specifically eastern Canada); however, parts of Europe and Russia also have the potential to be important source regions. In addition to these regions, Iizuka et al. (2018) argues for a small possible contribution of inorganic aerosols from remote regions such as East Asia and India, where emissions of anthropogenic SO_x, NO_x, and NH_3 are enormous (Crippa et al., 2016). Given that lifetimes of LG and DA in the atmosphere are estimated to be less than 10 days (Fraser and Lakshmanan, 2000; Hennigan et al., 2010; Lai et al., 2015), organic BB tracers originating from remote areas are unlikely to reach Greenland. Greenland is also unlikely to be a primary source region because most of Greenland is covered with ice sheets and is inhospitable to vegetation. Iizuka et al. (2018) calculated the regional

contributions of air mass origins to the SE-Dome and found that the contributions from North America are 2.5 times and 7 times larger than those from Europe and Russia, respectively (See pie diagram of Fig. 3.2a). Therefore, it is thought that North America (Canada) is likely the primary source region of the BB organic tracers. Our estimate based on the backward air mass trajectory is consistent with previous estimates of BB tracer source regions in the Greenland ice sheet (Legrand et al., 1992; Whitlow et al., 1994; Zennaro et al., 2014).

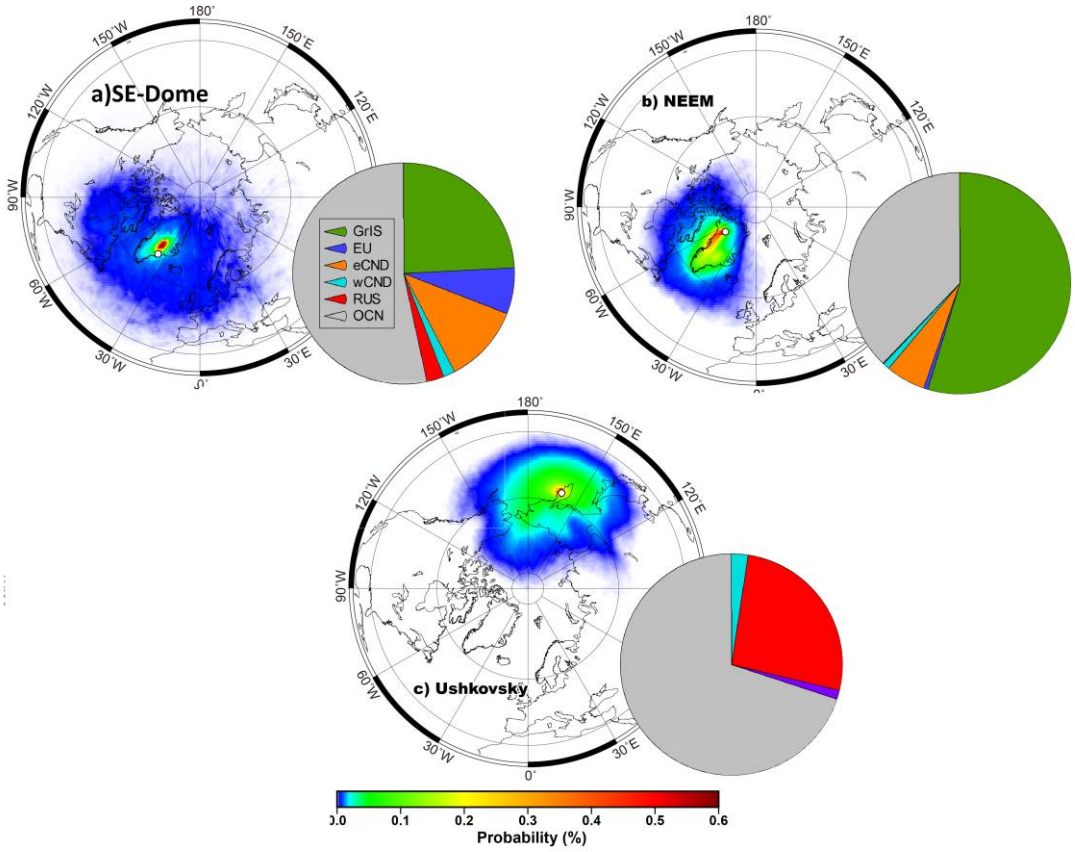

Figure 3.2. Probability distribution of air mass arriving at the **a)** SE-Dome, **b)** NEEM and **c)** Ushkovsky ice core site (10–1500 m a.g.l. as initial four points) from a 7-day 3D backward-trajectory analysis for the period of 1958–2014. A color scale indicating the probability percentage is shown at the bottom. Pie diagram shows the relative contribution of each region from where the airmass reached to ice core site. Abbreviations of the regions are shown in Fig. 1a except for ocean (OCN).

3. 3.2. Concentrations of the BB molecular tracers in SE-Dome ice cores

Historical changes in the record of the two BB tracers (LG and DA) in the SE-Dome ice core are shown in Figs. 3.4a–b. Concentrations of LG in the SE-Dome ice core range from below the detection limit (0.005 ng/g-ice) to 217 ng/L with an average of 18.27 ng/L, showing no clear increasing or decreasing trends toward the present with the occurrence of sporadic peaks in a handful of years. Conversely, concentrations of DA in the SE-Dome ice core range from below the detection limit (0.003 ng/g-ice) to 45 ng/L with an average value of 5.20 ng/L. Relatively higher concentrations of DA were recognized in the period of 1959–1964. A gradual increasing trend is observed from 2009 to 2014 （Fig. 3.4b).

To examine regional differences in the concentrations of LG and DA in the ice core, we compared the average values of the BB molecular tracer concentrations in different ice cores. Table 3.1 represents the average concentrations of LG and DA in the SE-Dome, NEEM (Zennaro et al., 2014), and Ushkovsky (Kawamura et al., 2012) ice cores for the same time interval. The NEEM ice core site is located on the northern part of the Greenland ice sheet, while the Ushkovsky ice core was collected from the Ushkovsky mountain glacier on the Kamchatka peninsula in far eastern Russia (Fig. 3.1b). The average concentrations of LG and DA in the SE-Dome ice core are lower than those in the Ushkovsky and NEEM ice cores (Kawamura et al., 2012; Zennaro et al., 2014), with the highest concentration found in the Ushkovsky ice core. Such differences are likely attributable to differences in the sources, the snow accumulation rates, and the atmospheric transport of BB tracers to the respective glacier sites (Müller-Tautges et al., 2016). The average LG and DA concentrations at the Ushkovsky ice core

site are approximately 5–30 times higher than those at the Greenland ice core sites (NEEM and SE-Dome). The higher concentration in the Ushkovsky ice core is unlikely to be explained by the difference in the enrichment effect due to the low accumulation rate, because the accumulation rate (0.87 m/yr) of the Ushkovsky ice core (Kawamura et al., 2012) is much higher than that of the NEEM ice core (0.22 m/yr). The higher concentrations of BB tracers in the Ushkovsky ice core likely reflect the greater magnitude of BB in the source regions and/or the site's proximity to the source regions. According to the air mass backward-trajectory analyses, the source of LG and DA in the Ushkovsky ice core is Siberia (in Russia) including Kamchatka (Fig. 3.2c) (Kawamura et al., 2012), while eastern Canada is likely the primary source of LG and DA in Greenland (Fig. 3.2). Siberia is one of the most intensive boreal forest BB regions (Giglio et al., 2013; Schultz et al., 2008; Scott et al., 2018). Emissions of BB aerosol tracers in Siberia are estimated to be several times higher than those in eastern Canada (Fig.3.1b) (Schultz et al., 2008; Scott et al., 2018).

However, the relatively low concentrations in the SE-Dome ice core compared to the NEEM ice core are unlikely to be explained by differences in the magnitudes of BB between the source regions because the possible sources of LG in the two Greenland ice cores are nearly the same region (Fig. 3.2a and b). This difference is likely instead to be due to a difference in the snow accumulation rates between the two sites. In fact, the snow accumulation rate at the SE-Dome site (1.01 m/yr) is approximately 5 times higher than that at the NEEM ice core site (0.22 m/yr) (Zennaro et al., 2014). Therefore, the dilution effect is significant for the SE-Dome site compared to the NEEM site. Based on these lines of analysis, differences in the concentrations of BB tracers for the

different ice core sites are likely explained by differences in the BB intensity between the potential source areas and the snow accumulation rates at the different sites.

Table 3.1. Mean concentrations of biomass burning tracers in ice cores.

Ice core	Period (AD)	LG (ng/L)	DA (ng/L)
SE-Dome (this study)	1958–2014	18.27±38.85	5.17±10.13
Ushkovsky (Kawamura et al., 2012)	1961–1997	542.6±861.8	101.53±99.77
NEEM (Zennaro et al., 2014)	1961–2001	98.26±84.97	–

3. 3.3. Assessment of BB tracers in the SE-Dome ice core

Ice core records of BB aerosol tracers are potentially affected by several factors, including the emission of the tracers from the source regions (Zennaro et al., 2014), changes in the wind regime (Kawamura et al., 2012), and precipitation (wet deposition) (Zennaro et al., 2014). To examine the primary factors that determine the concentrations of the BB tracers in ice cores, we compared our BB tracer annual record to BB records in the source region and to instrumental records of decadal-scale climate oscillations. In order to investigate seasonal dynamics of BB tracer records, we conducted seasonal resolution analysis in 2014 (Fig. 3.3).

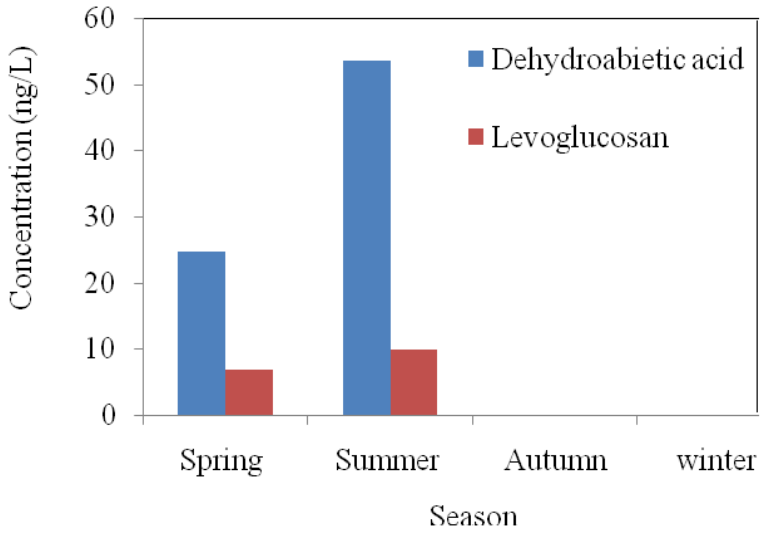

Figure 3.3: Seasonal variation of the BB tracer concentrations in SE-Dome ice core.

Snow accumulation rate in 2014 is extremely high compared to other years, allowing us seasonal analysis. In 2014, the BB tracer records show distinct seasonal trend with remarkable increase in concentration during spring and summer and very low concentrations in winter. This seasonal trend is consistent with the fact that natural BB events increase during the warm season (spring to summer) in boreal forests (Johnson, 1992; Macias Fauria and Johnson, 2008; Seki et al., 2015). This indicates that the BB tracers were transported and deposited in the ice sheet during warm season when forest fire is usually occurred. We do not discuss the effect of precipitation because diurnal resolution BB data, that are required to assess the precipitation effect on aerosol deposition, are not available.

Comparison with the BB record

To evaluate the extent that LG and DA in the SE-Dome ice core record BB events in Canada in the past and to further constrain the source regions of LG and DA, we compared the BB tracer data to the observationally based records of areas burned for all

types of vegetation fire （Fig. 3.4）in Canada. The area burned data were adapted and compiled from the National Forestry Database of Canada (http://nfdp.ccfm.org/index_e.php), Stocks et al.（2002) and Macias Fauria and Johnson (2008). In addition, area burned data of Canada (Fig. 3.4c) from the Global Fire Emission Database version 4.1s (GFED4.1s) were used for comparison. Area burned data from the National Forestry Database and Stocks et al.（2002) (Fig. 3.4c) covers the entire period (1958–2014) recorded by the SE-Dome ice core. Conversely, the area burned data in GFED4 (Fig. 3.4d) is limited to the period of 1997–2014. The area burned data from the National Forestry Database and Stocks et al.（2002) are not complete nor without some limitations. The data have been collected by different agencies. Therefore, the data completeness and quality may vary among agencies and years. Conversely, GFED4, which is used to reconstruct the area burned caused by BB, combined satellite information on fire activity and vegetation productivity to estimate the gridded monthly burned area and fire emissions; in addition, it used scalars to calculate higher temporal resolution emissions. Note that the area burned data used in this study account for burning events over all of Canada including the western region, which is not one of the potential source areas of the BB tracers in the Greenland ice core for most years, as inferred from the air mass backward trajectory (Fig. 3.2).

Our LG record shows large fluctuations over the past 60 years with sporadic high peaks in 1961, 1964, 1994, 1998, and 2013 with the largest peak in 1964 (Fig. 3.4a). Conversely, the DA record in the SE-Dome ice core shows marked peaks in 1961, 2003, 2010, 2013, and 2014. The burned area data in Canada (Figs. 3.4c and 3.4d) also show a number of pronounced peaks in 1961, 1981, 1989, 1994, 1995, 1998, 2004, 2010, 2013,

and 2014. Six significant BB events in Canada during the past 60 years are found to correspond to the BB tracer peaks in the SE-Dome ice core. This correspondence suggests that the BB molecular tracers in the SE-Dome ice core document approximately 60% of the significant BB events in Canada over the last 60 years. This relatively high correspondence between the ice core record and the BB events in Canada suggests that analyses of BB molecular tracers in Greenland ice cores are useful to reconstruct the frequency of BB events in certain regions of Canada.

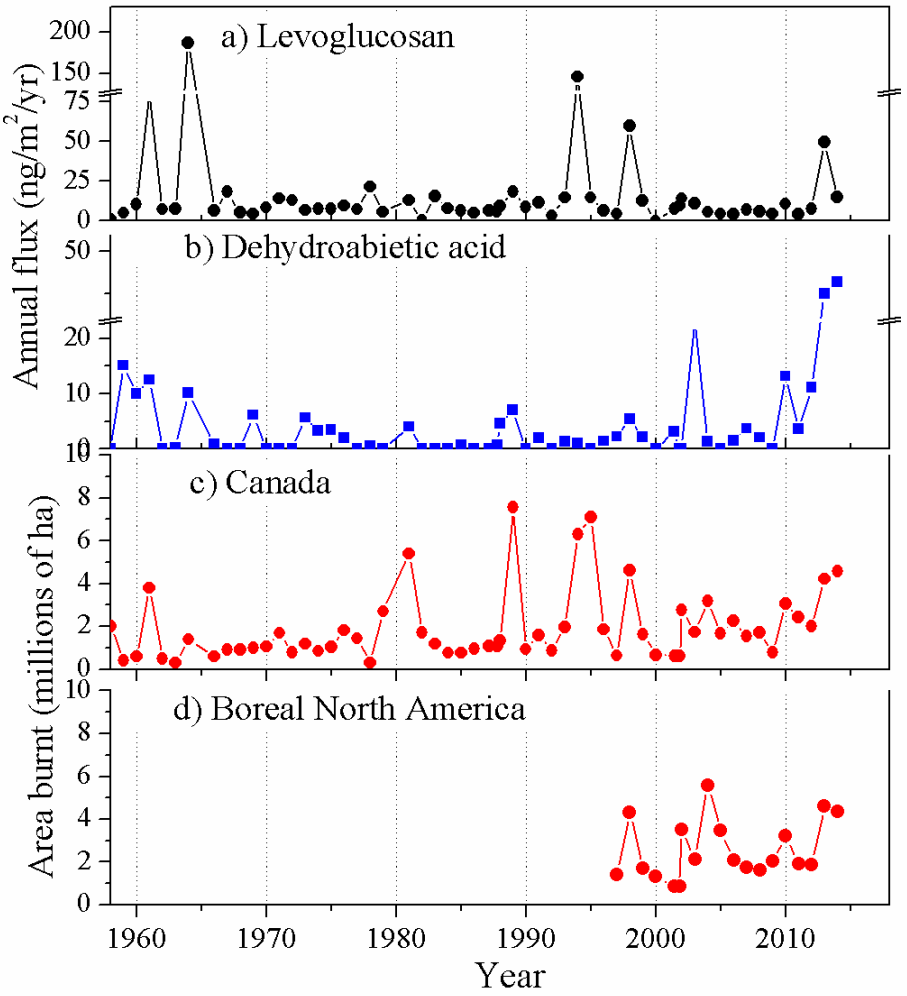

Figure 3.4: Historical changes in the annual flux of (a) levoglucosan (LG) and (b) dehydroabietic acid (DA) in the SE-Dome ice core together with (c) the annual area burned in Canada（data adapted and compiled from the National Forestry Database (http://nfdp.ccfm.org/index_e.php), Macias Fauria and Johnson (2008) and Stocks et al. (2002)）and (d) the annual area burned due to vegetation fires in boreal North America (BONA) from 1997 to 2014 (http://www.globalfiredata.org/analysis.html). In GFED4, the continents have been divided into 14 basic regions to represents the BB data on a regional basis, where Canada is considered to be BONA.

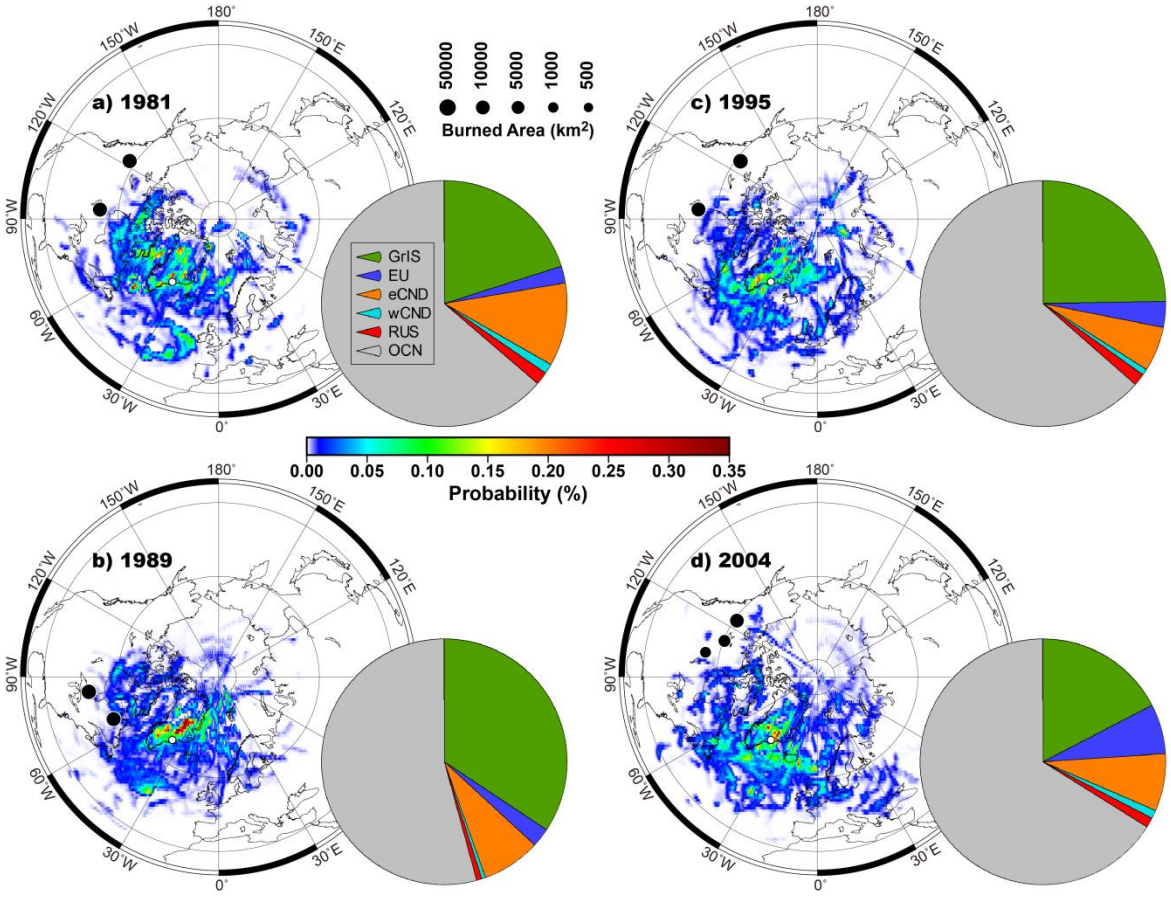

Figure 3.5: Probability distributions of an air mass arriving at the SE-Dome site (10–1500 m a.g.l. as initial four points) from a 7-day 3D backward-trajectory analysis in the spring-summer seasons of (a) 1981, (b) 1989, (c) 1995 and (d) 2004, when BB events were prominent in Canada but the events were not recorded in the SE-Dome ice core LG and DA data. Pie diagrams show the relative contribution of each region from where the airmass reached to the SE-Dome ice core (abbreviations as of Fig. 3.1). Black dots represent the regions where significant BB occurred in those years and the size of the black dots indicates the magnitude of area burnt.

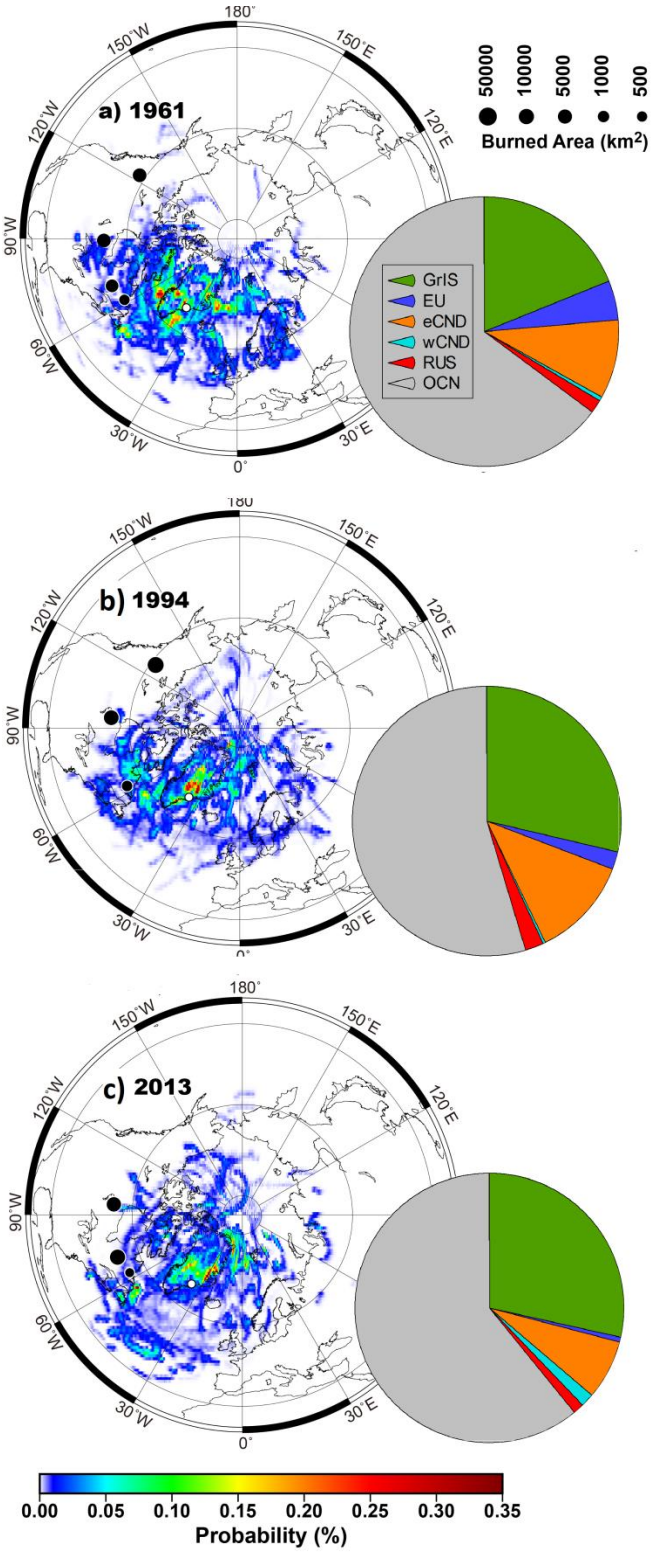

Figure 3.6. Probability distributions of an air mass arriving at the SE-Dome site (10–1500 m a.g.l. as initial four point) from a 7-day 3D backward-trajectory analysis in the spring - summer season of (a) 1961, (b) 1994 and (c) 2013, when BB events were prominent in Canada and the LG and DA records in the SE-Dome ice core also show prominent peaks. Pie diagrams show the relative contribution of each region from where the airmass reached to the SE-Dome ice core (abbreviations as of Fig. 3.1). Black dots represent the regions where significant BB occurred in those years and the size of the black dots indicates the magnitude of area burnt.

However, the four BB events in 1981, 1989, 1995, and 2004 were not registered in the SE-Dome ice core records of the BB molecular tracers (Figs. 3.4a–d). These mismatches suggest that LG and DA in the Greenland ice core do not record all the BB events in Canada. One possible explanation for the absence of BB signals in the ice core BB tracers is that these BB events took place in regions from which the emitted BB tracers could not reach the SE-Dome. Indeed, the prominent BB events in 1981, 1989, 1995, and 2004 were found to have primarily taken place in the western region of Canada (Stocks et al., 2002). To further examine the observed mismatch between the ice core record and the observational based BB events, we calculated the probability distributions of the 7-day backward trajectories for the spring-summer seasons (six months from March to August) in the selected years (Fig. 3.5). As shown in Fig. 3.5, the air masses indeed did not come from the significant BB areas in the mismatched years within the last 7 days.

Conversely, in 1961, 1994, 1998, 2010, 2013, and 2014, the air masses came from regions (Fig. 3.6) where significant BB events occurred （http://nfdp.ccfm.org/fires/national_e.php）. The 7-day air mass backward-trajectory analysis suggests that air masses originating in the eastern part of Canada (i.e., Newfoundland, Quebec, Ontario, and some parts of Manitoba） reached the SE-Dome ice core site during those years. Therefore, our result demonstrates that the registration of BB events in Greenland ice cores strongly depends on the origin of the air masses being transported to the ice core site.

Other discrepancies between the ice core and the BB events in Canada are observed in 1964 and 2003. In these years, significant peaks in LG and DA were

recognized in the ice core while prominent BB events were absent in Canada (Fig. 3.4). However, a closer look reveals that, even though the total area burned peak for all of Canada is small in 2003, the burned area peaks in the eastern part of Canada (Ontario and Manitoba) were relatively high （http://nfdp.ccfm.org/fires/national_e.php）. In addition, the probability distribution of the trajectory analysis shows that 29% of the air mass arriving at the SE-Dome site in the spring of 2003 came from Canada, which includes Quebec, Ontario, and Manitoba. Therefore, the significant DA peak in 2003 may reflect local BB events in Ontario and Manitoba.

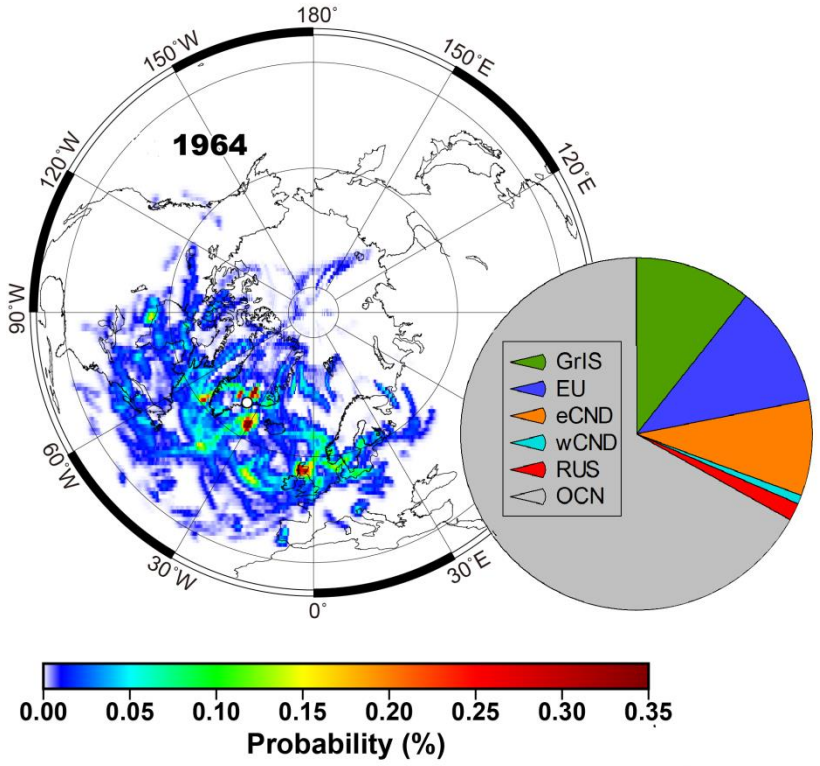

Figure 3.7: Probability distributions of an air mass arriving at the SE-Dome site (10–1500 m a.g.l. as initial four point) from a 7-day 3D backward-trajectory analysis in the spring -summer season of 1964. Pie diagrams show the relative contribution of each

region from where the airmass reached to the SE-Dome ice core (abbreviations as of Fig. 3.1).

As for 1964, the source region of the LG peak remains unclear because there were no significant area burned events in any region in Canada. One possible explanation for the mismatch is that the BB tracers originated from regions other than Canada such as the Greenland and Europe in 1964. The probability distribution of the 7-day air mass backward trajectory for 1964 （Fig. 3.7）shows that a significant portion of the air mass came from Greenland (11%) and Europe (11%) in spring to summer. However, most area of the Greenland is covered with ice and is inhospitable to life forms. As for Europe, the number of fires and area burned is reported to be prominent in East Germany in that year (Goldammer and Mutch, 2001) and fire weather index is also high in Europe during 1960-1965 (Venäläinen et al., 2014). Hence, the LG peak in 1964 might reflect fire event in Europe. Conversely, it is noteworthy that in 1964, high concentrations of NH_4, which is also considered as a BB tacer, also been found (Iizuka et al., 2018).

Our data shows no correlation between LG and DA in the SE-Dome ice core, even though coniferous trees are more numerous than deciduous trees in Canada. Such a decoupling of LG and DA is also found in the Ushkovsky ice core (Kawamura et al., 2012). This indicates that the LG originated from other sources, such as deciduous trees, brown coal, and agricultural wood, rather than coniferous trees (Oros and Simoneit, 2000; Simoneit et al., 1999). An alternative explanation is the preferential degradation of DA during the transport process and after deposition onto ice sheet. The aromatic structure of DA has a higher sensitivity to photodegradation than LG (V. Elias et al., 2001; Simoneit, 2002). LG is also thought not to be significantly degraded in the early

firnification process (Kehrwald et al., 2012). In addition, a lack of covariance between DA (tracers of conifer resin burning) and LG (cellulose burning tracers) may imply that conifer tree barks are more readily burned than woody parts during BB events (Eichler et al., 2011).

Effect of decadal-scale climatic oscillations on BB aerosol tracer transportation

Next, we examine the influence of changes in the decadal-scale atmospheric circulation on aerosol transport. Changes in the wind regime affect the atmospheric transport of aerosols. For example, sources of aerosols in East Asia are dramatically changed due to seasonal changes in the Asian monsoon circulation (Kawamura et al., 2003). Decadal-scale changes in the wind regime may also influence the transport of aerosols. The Arctic Oscillation (AO), which is a key feature of climate variability in the studied region, may influence the transport of aerosols to high latitude regions (Fu et al., 2016; Seki et al., 2015). The AO refers to an opposing pattern of pressure between the Arctic and the northern middle latitudes. When the AO index is positive, the surface pressure is low in the polar region, which helps the middle latitude jet stream blow strongly and consistently from west to east and induces warmer air to move northward from the mid-latitudes (Thompson and Wallace, 1998). Conversely, when the AO index is negative, the opposite situation occurs. Seki et al. (2015) postulated that a positive AO might intensify the long-range transport of BB aerosols from their source regions to ice core sites via the westerly jet. The Atlantic Multi-decadal Oscillation (AMO) is a variability in the North Atlantic sea surface temperatures with a periodicity of 60–80 years (Kerr, 2000) and might also influence the transport of aerosols around Greenland. The AMO coupled with the atmosphere may trigger the AO to vary on a multi-decadal

time scale (Polyakova et al., 2006), control the position of the westerly jet, and potentially affect aerosol transport around Greenland.

Because BB usually occurs in warm season, we compared our BB tracer records of the SE-Dome ice core to the warm season AO and AMO indices to examine the extent to which ice core records are linked to climate oscillations. The LG record is moderately correlated to the warm season AO ($R= 0.42$, $p<0.001$), while DA exhibits no correlation （Figs. 3.8a and b). However, we found no correlation of either BB tracer records with the AMO. These results suggest that changes in the climatic oscillations do not significantly influence the transport of BB tracers that originate in eastern Canada. Hirdman et al. (2010) also argued that changes in the atmospheric circulation can only explain a small fraction of the long-term trends in the BC loading in the Arctic and that changes in the emissions from the source regions primarily dominate these trends.

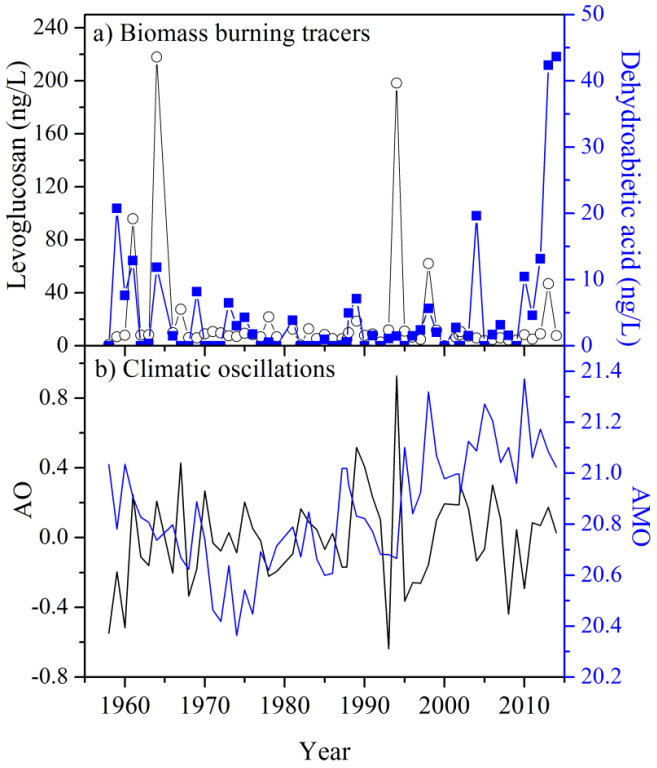

Figure 3.8: (a) Historical trends in the concentrations of levoglucosan (LG) (black open circle) and dehydroabietic acid (DA) (blue solid square) in the SE-Dome ice core. (b) Instrumental records of the warm season Arctic Oscillation (AO) index (black line) (https://www.ncdc.noaa.gov/teleconnections/ao/) and the Atlantic Multi-decadal Oscillation (AMO) index (blue line) (http://www.esrl.noaa.gov/psd/data/timeseries/AMO/) during the period from 1958 to 2014.

3.4. Conclusions

We generated for the first time continuous records of BB molecular tracers over the last 60 years from a well-dated Greenland ice core (SE-Dome) and assessed the BB

molecular tracers in the ice core. A comparison of our ice core tracer records with those of other ice cores indicates that concentrations of BB tracers in ice cores likely reflect differences in the BB magnitude in the source area and that the snow accumulation rate likely has an influence. LG and DA data in the SE-Dome ice core record most of the BB events in eastern Canada from 1958 to 2014, suggesting that ice core analyses of LG and DA in Greenland ice cores are a promising approach to reconstruct the BB frequency in eastern Canada, even though some BB events in Canada are not reflected in the ice core LG and DA records because these records also depend on the origins of the air masses reaching the ice core site. Decadal-scale climatic oscillations such as AO and AMO do not appear to significantly influence the transport of BB tracers. The apparent discrepancy between LG and DA suggests that along with boreal forest fires, other BB events, such as agricultural wood burning, deciduous plant burning, and coal combustion, are also important sources of the LG preserved in the SE-Dome ice core.

Chapter 4

Reconstruction of boreal forest fire history of North America for the last 300 years using ice core record

In this study, we measured two organic biomass burning tracers (levoglucosan and dehydroabietic acid) in Aurora peak and Sigma-D ice cores collected from the southern Alaska and northwestern Greenland to reconstruct changes in fire frequency of boreal forest in the North America and investigate its link to climate change. Air mass backward trajectory analysis suggests that biomass burning tracer records in the Aurora peak and Sigma-D ice cores reflects loadings of boreal forest fire aerosol from western and eastern part of North American boreal forest area, respectively. The both ice core records show that significant boreal forest fire events happened frequently in the regions since Little Ice Age. Increase in dehydroabietic acid in the recent decades in both the ice cores indicates that coniferous tree burning has been increased in that regions in the recent decade. Prominent peaks of biomass burning tracers well correspond to the climate warming periods. This indicates that temperature is the major driver to intensify the boreal fire event on decadal timescales. In addition, changes in the decadal scale climate oscillations such as North Atlantic Oscillation (NAO), likely exert an influence on fire dynamics in eastern Canada, by increasing aridity. On the other hand, strong link between decadal scale climate oscillations and boreal fire is not recognized in the western boreal region over the past 300 years. The coupling of boreal fire and regional temperature for the last 300 years, suggest that occurrence frequency of boreal forest fire will increase in a future due to the ongoing global warming.

4. 1. Introduction

Understanding the fire regimes in boreal forest is important as, it contains one third of world's forests, with half of the world forest carbon (Conard et al., 2002) and is an important souce of air pollutants throughout the Arctic (Lavoué et al., 2000; Quinn et al., 2008). In addition, BB in the boreal forest is a matter of concern, as the boreal regions are at the lattitide, where most of the global warming are predicted to occur (Hansen et al., 2010). In the past several decades, changes in regional climate patterns led to the increase of boreal forest fire in Canada and Alaska (Calef et al., 2015; Kasischke and Turetsky, 2006). Interannual forest fire variability in Siberia during the last two decades is thought to be caused by a combination of the Arctic Oscillation (AO) and regional summer temperatures (Balzter et al., 2005). However, understanding the impact of climate on the boreal forest fire over the last two or three decades are not sufficient to clearly assess the impact of climate change on boreal fire regimes. Hence, it is important to reconstruct long-term variability of boreal forest fire to improve prediction of the impact of future climate changes on boreal fires.

Charcoal data from lake and peat sediments as well as ice core BB records show a link between wildfires and climate on decadal to centennial time scales (Marlon et al., 2012; Seki et al., 2015; Zennaro et al., 2014). Sedimentary charcoal record, which is primarily produced from BB (Whitlock and Larsen, 2001), represents very local fire history (Waito et al., 2018b). Siberian boreal forest fire history has been reconstructed using the organic BB tracers records (including LG and DA) from Ushkovsky ice core, Kamchatka, Russia. This ice core record shows empirical link between fire and regional climate (Kawamura et al., 2012; Seki et al., 2015). However, North American and Eurasian boreal fire regimes are different from that of Siberia due to the differences in

the vegetation, weather pattern and fire ecology between the two boreal regions (de Groot et al., 2013; Wooster, 2004). On the other hand, Zennaro et al., (2015) reconstructed fire history in North America over the last 2000 years based on LG, BC and ammonia analyses in Greenland ice core. However, BC and ammonia can be emitted from other sources (IPCC, 2013b; Legrand et al., 1992). Moreover, McConnell et al., (2007) stated that, after 1850, BC deposited in Greenland ice sheet are mainly originated from industrial emission. As for LG, which is produced solely from BB (Nolte et al., 2001; Simoneit et al., 1999), this author analyzes very few samples for the last 300 years to clearly assess the fluctuation in the fire history in North America during the recent centuries and the impact of climate warming on forest fire. Additionally, interpreting the fire history using the BB tracers record in Greenland ice core cannot represents the fire history of the entire North America/Canada, rather Greenalnd ice core represents the fire history of only eastern Canada (Parvin et al., 2019). Reconstruction of boreal forest fire history of North America over the last few hundred years is decisive, as it provides opportunity to investigate the changes in fire at different phases (Little Ice Age (LIA)-industrial revolution-recent days).

In this study, we reconstructed the boreal fire history in North America over the past few hundred years based on analyses of LG (BB tracer) and DA (conifer tree burning tracer) in the two ice cores collected from Alaska and Greenland to understand the fire history in eastern and western part of boreal forest in North America. Furthermore, we evaluated how past climate change affected boreal forest fire in North America.

4.2. Sampling sites description

Aurora Peak (63.52°N; 146.54°W, 2825m a.s.l., core length~180m), and Sigma-D (77.636 N, 59.120 W, 2100m a.s.l., core length~225m) ice cores were collected from southeast of Fairbanks, Alaska and Northwestern part of Greenland, respectively (Fig. 4.1). Aurora peak ice core has been drilled in 2008 while Sigma-D ice core has been collected in 2014. The detail information of ice core drillings and chronologies are given by previous studies (Matoba et al., 2015; Pokhrel et al., 2016). The snow accumulation rates in Aurora peak and Sigma-D ice core are 0.60 m/yr and 0.32 m/yr, respectively. The snow accumulation rates in these two ice cores are relatively low compare to SE-Dome ice core. Hence, those ice cores do not allow us to generate high resolution record. We have analyzed one sample per 4-4.5 years to reconstruct boreal fire history over the past 300 years.

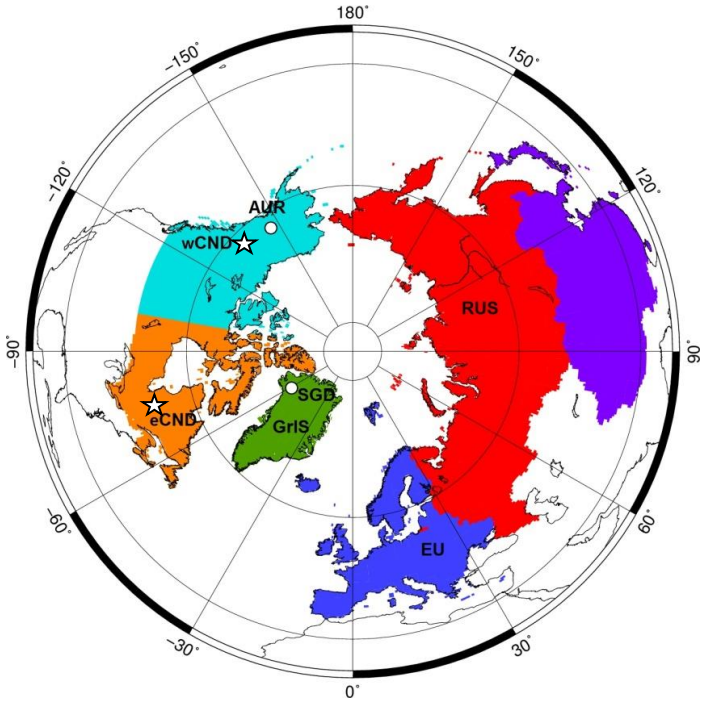

Figure 4.1: Map showing the location of the Sigma-D (SGD) and Aurora peak (AUR) ice core in the Northern Hemisphere and five regions for calculating regional

contribution (GrIS: Greenland, EU: Europe, RUS: Russia, wCND: western Canada+Alaska, eCND: eastern Canada). The stars indicate the location of tree ring sites used to reconstruct the summer temperature (Gennaretti et al., 2014; Szeicz and MacDonald, 1995).

4.3. Results and discussion

4.3.1. Source area assignment for boreal forest fire emitted aerosol in the ice cores

We conducted the probability distribution of the integrated 7-days airmass backward-trajectory analysis during the period from 1958 to 2013 to infer source regions of the BB tracers preserved in the studied ice cores, since life time of LG and DA in the atmosphere are estimated to be less than 10 days (Fraser and Lakshmanan, 2000; Hennigan et al., 2010; Lai et al., 2015). The probability distributions have been calculated using the method described elsewhere (Iizuka et al., 2018) and briefly in chapter 2. Probability distribution of 7-days airmass backward trajectory analysis indicates that eastern Canada and some parts of western Canada is likely the main source region of the BB tracers in Sigma-D ice core (Fig. 4.2a). On the other hand, western part of Canada and Alaska is found to be the main source region of DA in Aurora peak ice core (Fig. 4.2b). In addition, some portions of Russia are also potential source region. These results indicate that BB tracers records in Sigma-D and Aurora Peak ice core reflects BB aerosol loadings mainly from Canada and Alaska, respectively.

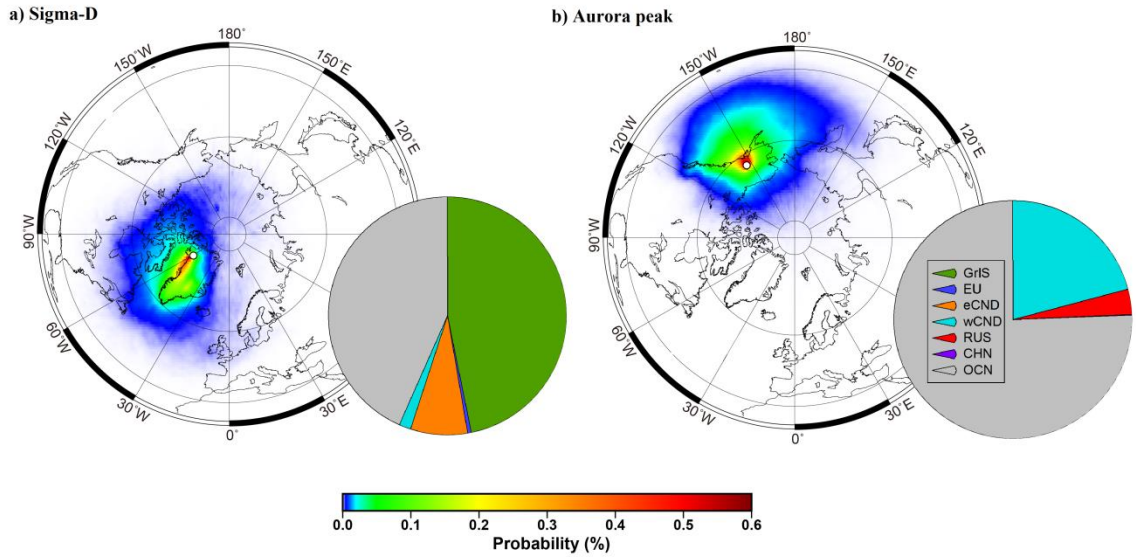

Figure 4.2. Probability distribution of an air mass arriving at the Sigma-D (a) and Aurora peak (b) ice core (10–1500 m a.g.l. as initial four points) from a 7-day 3D backward-trajectory analysis for the period of 1958–2013. A color scale indicating the probability percentage is shown at the bottom. Pie diagram shows the relative contribution of each region from where the airmass reached to ice core sites. Abbreviations of the regions are shown in Fig. 4.1 except for ocean (OCN).

4. 3.2. Historic records of levoglucosan and dehydroabietic acid

The LG and DA time series in Sigma-D and Aurora peak ice cores exhibit decadal time scale variability for the last 300 years (Figs. 4.3a and b), indicating that frequency of boreal forest fire have been dramatically changed in North America over the last few hundred years. The boreal forest fire is usually caused by naturally (lightning) or through direct human ignition (Stocks and Martell, 2016). To examine the influence of human population growth on BB in Canada and Alaska, we compared the

ice core BB tracers data with population data of Canada (Statistics of Canada) and Alaska (Resident Population Data - 2010) (Fig. 4.3c).

Our Aurora peak ice core record shows several high peaks of BB tracer concentrations during LIA (1725 to 1800). Such sporadic high peaks are also observed in BB tracer record of Sigma-D ice core during the LIA. Those results indicate that intense BB events held in the entire region of boreal forest in North America during LIA. Few sporadic high peaks of BB tracers has been found in both of the ice core records during 1880 to 1925, which is regarded as the period of industrial revolution in Canada (Anastakis, 2017). The BB events during 1880-1925 are probably caused by human activity, as human ignition is considered as a major cause of forest fire after the industrial revolution (Campos-Ruiz et al., 2018; Marlon et al., 2012). During the industrial revolution in Canada (1860-1950), several accidental forest fire events have been documented, when they constructed rail roads and industry by clearing the forest (Anastakis, 2017).

Furthermore, the DA concentrations in Aurora peak ice core show an increasing trend from 1989 to present (2008). This recent increase is consistent with the increased rate (2.4% yr^{-1}) of BB in Alaska over the last 50 years (Calef et al., 2015), confirming robustness of our approach. Similar increasing trend towards the present has also been observed in the DA and LG records in Sigma-D ice core. This recent increasing trend of the tracers in Sigma-D ice core well corresponds to the SE-Dome ice core records. Although population has linearly increased toward the present in Canada and Alaska (Fig. 4.3c), from 1970 to present days, resource management agencies of Canada have taken different wildfire suppression policies (Stocks and Martell, 2016) to reduce the severity of fire. Conversely, it has been reported that, in Canada and Alaska, during the

last 60 years, more than 70% of the forest fires have been held due to lightning (Stocks et al., 2002; Veraverbeke et al., 2017). Hence, the lightning ignition is a high degree of probable cause for recent increase in boreal fire in east and western part of Canada, as well as in Alaska.

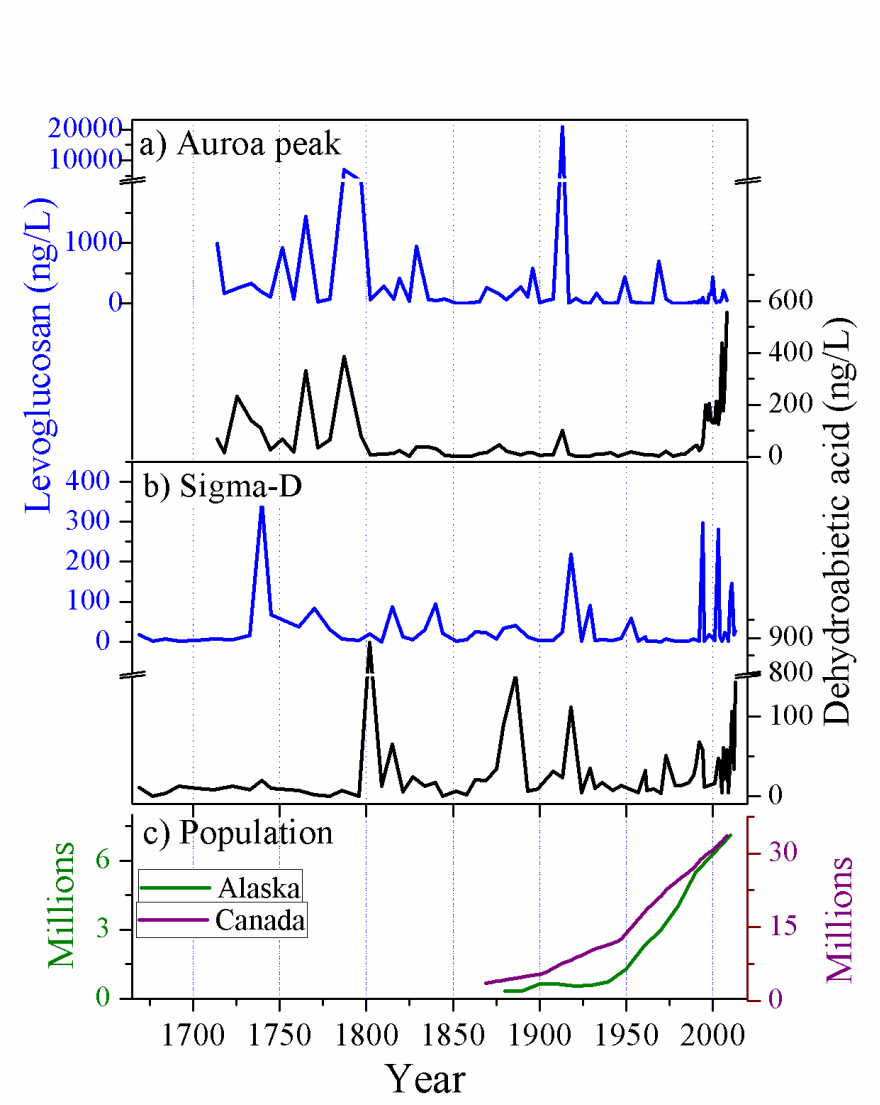

Figure 4.3: Temporal variations of the BB tracers in the two ice cores together with population growth. a) Changes in LG and DA concentrations in Aurora peak ice core from 1714 to 2008. b) Changes in LG and DA concentrations in Sigma-D ice core from

1669 to 2013. c) Population estimates for Canada (Statistics of Canada) and Alaska (Resident Population Data - 2010) .

4.3.3. Comparison between the levoglucosan and dehydroabietic acid records

LG records do not correlate with that of DA in both of the ice core records. Similar trend has also been observed in Ushkovsky (Kawamura et al., 2012) and SE-dome (Parvin et al., 2019) ice core records. It has been reported that concentration of DA is lower than that of LG in the air and ice (Haque et al., 2016; Kawamura et al., 2012; Parvin et al., 2019). In both of the ice core records, concentrations of LG are very high in some years compared to that of DA. The possible reason for relatively high LG concentration is that LG may originates from other sources such as deciduous trees, brown coal and agricultural wood in those years rather than coniferous trees (Oros and Simoneit, 2000; Simoneit et al., 1999). However, concentration of DA is found to be higher than that of LG in some years (in Sigma-D: 1802, 1886, 2013; in Aurora peak: 1995-2008). It depends on what types of tree species are burning. For example, burning of Douglas fir, Lodgepole pine, Ponderosa pine, Sitka spruce and Western white pine, that are very common tree species in some regions of Canada, emits more DA than LG into the atmosphere (Simoneit et al., 1999). Again, the emission of DA likely differs from species to species in conifer trees. DA was found to emit in higher concentration from the burning of White pine trees compared to Hemlock and Balsam fir trees (Fine et al., 2002a). Atmospheric life time of these tracers is also a factor for varying the concentration of the two tracers in the same year (V. O. Elias et al., 2001; Simoneit, 2002).

4.3.4. Comparison to other biomass burning proxy record

Since charcoal is emitted solely from BB and is well deposited and preserved in lake sediment, it serves as a record of fire history (Ali et al., 2012). Hence, we compared our BB tracer records in ice cores with charcoal record in sediment cores. Aurora peak ice core records are compared with charcoal record in the Paradox lake sediment, Alaska (Anderson et al., 2006), while the BB tracer records in Sigma-D ice core are compared with charcoal record in eastern Canada lake sediment (Québec) (Lafontaine-Boyer and Gajewski, 2014). Charcoal deposition is expressed in accumulation rate as sedimentation rates varied significantly over time (CHAR; particles/cm^{-2}/yr^{-1}). LG and DA records in Aurora peak have some similarities with the charcoal records, but also show considerable differences (Fig. 4.4a). Similar to Aurora peak ice core, charcoal record in Alaska also shows prominent peaks in LIA. However, from 1850 to recent ages, there is a dissimilarities between the two records. Conversely, few big peaks (1880 to 1925) of the BB tracers in Sigma-D ice core is recognized in Quebec charcoal record, but other peaks in Sigma-D record are not observed in the charcoal record (Fig. 4.4b).

The possible explanation of the mismatch between the two records is that, sedimentary charcoal data reflects the local fires (Clark and Royall, 1996; Schüpbach et al., 2015). It has been reported that charcoal deposited in lake system is originated from the tree burning within approximately 500 m radius of the lake (Waito et al., 2018a), whereas BB tracers in ice core reflect regional scale fire events (approximately 2-3 thousand kilometers in radius) (Elias et al., 2001; Kawamura et al., 2012; Parvin et al., 2019). Another possible reason is, chronologies of charcoal record generally have much large uncertainties than that of ice cores (Grieman et al., 2018). Apart from those

reasons, one important caveat to this comparison is that the time resolutions of sedimentary charcoal records (30-35 samples/ 300 years) are lower than those of ice cores (70-80 samples/300 years). It is noteworthy that recent year's records of ice core BB tracers well agree with observational record of area burnt in Canada and Alaska. These lines of analyses prove the robustness of the LG and DA over charcoal record as BB tracer.

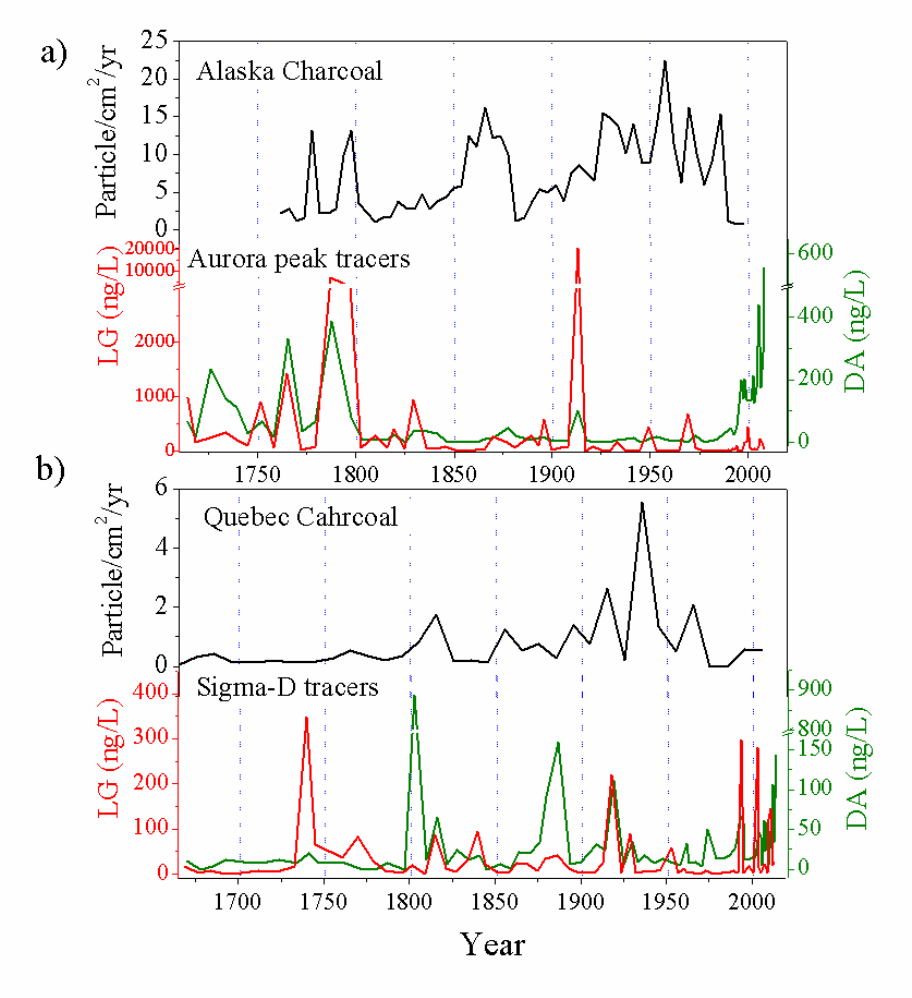

Figure 4.4: Comparisons of BB tracers in the ice core with the charcoal record in sediment core for the same time period. a) Comparison of LG and DA in Aurora peak ice core with Charcoal accumulation rate in lake sediment, Alaska (Anderson et al.,

2006). b) Comparison of LG and DA in Sigma-D ice core with Charcoal accumulation rate in lake sediment of Quebec, Eastern Canada (Lafontaine-Boyer and Gajewski, 2014).

4.3.5. Climatic influences on decadal scale fire regimes in North America

Several factors i.e. humidity and temperature affect forest fire (Grieman et al., 2016; Seki et al., 2015). Temperature is thought to be one of the major drivers of BB in South Western USA for centennial timescale, as fire activity often intensified with warming (Marlon et al., 2009). The boreal forest fires are an important source of air pollutants throughout the Arctic (Zennaro et al., 2014). It is vital to investigate the influence of decadal scale changes in temperature on boreal forest fire in North America. Hence, we compare the changes in BB tracer records in both of the ice cores with dendroclimatic reconstructed summer temperature records in proximal regions over the past 300 years (Fig. 4.5).

Prominent peaks of LG and DA in Sigma-D ice core have been found during the periods when summer temperatures is also relatively high in Eastern Canada (Gennaretti et al., 2014) (Fig. 4.5a). Conversely, the prominent peaks of the BB tracers in Aurora peak ice core during LIA and the recent increasing trend of DA record well correspond to the decadal scale changes in temperature record in north Western Canada (Szeicz and MacDonald, 1995) (Fig. 4.5b). These coupling between the local temperature and BB tracer records suggest that warming is the major driver for intensifying the forest fire events in Canada and Alaska. These observations match with the recent findings of Ushkovsky ice core's BB tracer record in Kamchatka, Russia which showed empirical link with summer temperature in Northern Siberia for the last few hundred years (Seki

et al., 2015). In boreal regions, increasing temperature led to an extension of the length of fire season and a decrease in moisture level (Ali et al., 2012; Wendler and Shulski, 2009). It has been also reported that lightning ignition is also increased by warming (Veraverbeke et al., 2017). Hence, based on our findings and previous studies, it can be inferred that for the last few hundred years, regional climate warming act as the major driver for large wildfires in the boreal region, through lengthening of the fire season, fuel drying and increasing the rate of lightning fire occurrence.

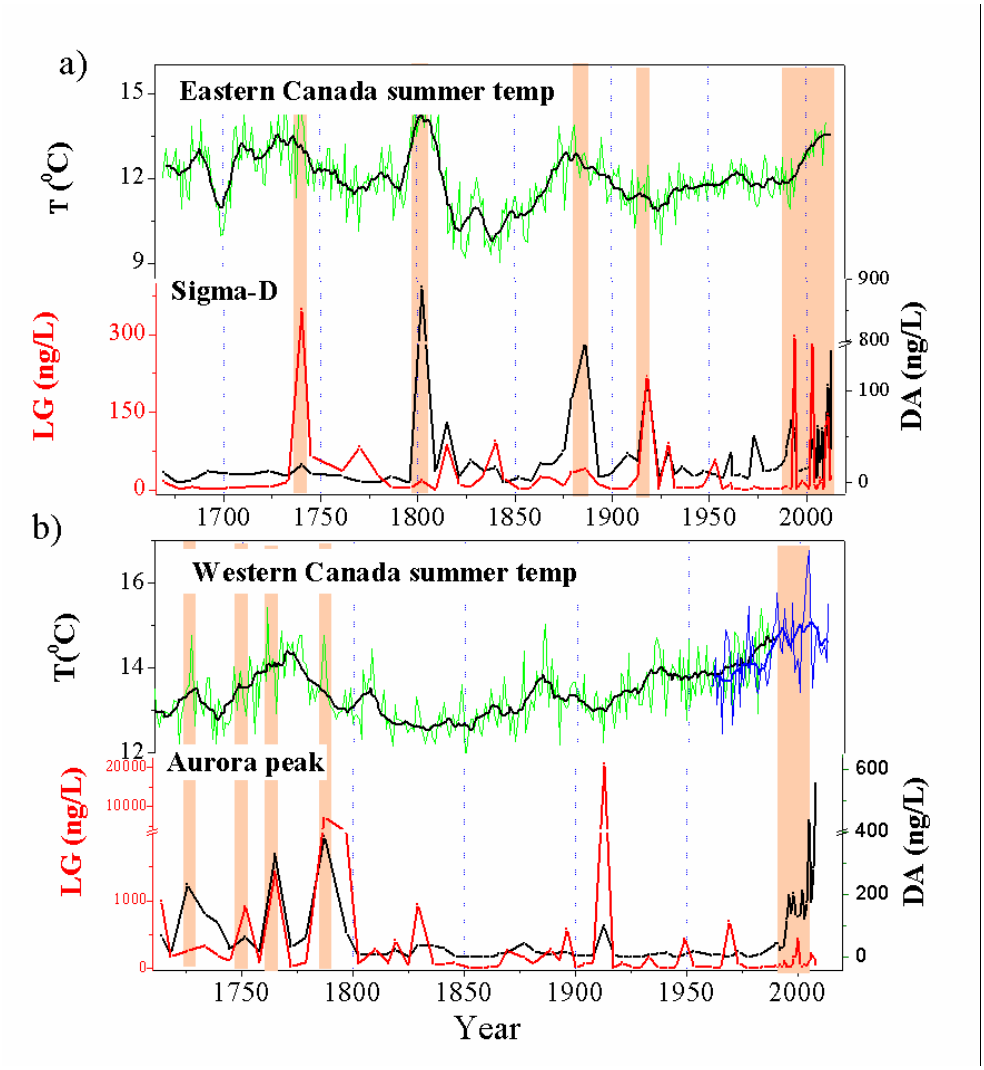

Figure 4.5: Comparisons of BB tracers in ice core with the dendroclimatic reconstruction of summer temperature for the same time interval. a) Comparison of LG and DA records in Sigma-D ice core with reconstructed summer temperature record in eastern Canada (Gennaretti et al., 2014). b) Comparison of LG and DA records in Aurora peak ice core with reconstructed summer temperature record in northwestern Canada (Szeicz and MacDonald, 1995). The black lines in the temperature records indicate the 10 years average value. The blue lines in figure b represent the instrumental values of temperature. The orange shading represents the periods when the BB tracer records have prominent peaks and temperature is also relatively higher.

Furthermore, decadal scale climatic oscillations also influence regional warming and drying (Folland et al., 2009; Mantua., 2001; Thompson & Wallace, 1998), which in turn can intensify the forest fire. The North Atlantic Oscillations (NAO) is a major mode of climate oscillation in the North Atlantic region, characterized by changes in the pressure gradient between the subtropical (Azores) high and the subpolar low (Hurrell et al., 2001). When the NAO index is positive, below-normal heights and pressure remain across the high latitudes of the North Atlantic and above-normal heights and pressure over the central North Atlantic, which enhance westerlies transporting warm air through central Canada to Europe. Hence, when the NAO index is well above zero (positive phase), weather will be dryer than normal over North-West Europe and eastern Canada (Folland et al., 2009). As eastern Canada is the major source region for the forest fire product deposited in Sigma-D ice core (Fig. 4.2a), we compare Sigma-D ice core BB tracer records with reconstructed summer NAO (Luterbacher, 2001) (Fig. 4.6a). Prominent peaks of BB tracers in Sigma-D ice core are found during the years when summer NAO is in positive phases (Luterbacher, 2001), except for some years (2005-2010). The possible explanation for this correspondence is that positive phases of summer NAO reduces the precipitation in eastern Canada (Folland et al., 2009) and this results in drying of fuels and created high fire hazard.

Pacific Decadal Oscillation (PDO) is a long-lived Pacific climate variability. When the PDO is positive, sea surface temperatures are anomalously cool in the interior of North Pacific and warm along the Pacific Coast (Mantua., 2001). The warm phases of PDO influence the large lightning fires in western Canada (1959-1999), and causes anomalously dry condition in the interior of Alaska and anomalous warming in the northwestern part of North America during summer (Macias Fauria and Johnson, 2008,

2006). It has been reported that the recent (last 50 years) increase of area burnt in Alaska is attributed to climate change and intensified by the PDO's positive shift in the middle of the existing fire (Calef et al., 2015). Hence, we compare our tracers record in Aurora peak ice core with the reconstructed PDO record (MacDonald, 2005) for the last 300 years (Fig. 4.6b). The comparison revealed that the concentrations of BB tracers in Aurora peak ice were high in few years during the positive phases of PDO, except for 1750 and 2000-2008. This finding is consistent with the modern observations (Calef et al., 2015) that decadal frequencies of area burned in the western Canada and Alaska (1959 to 1999) correlate with PDO and large lightning fire occurrence may have increased during the positive phases of PDO. The correspondence between PDO and BB tracer record suggests that decadal scale changes in PDO exert an indirect influence on amplification of boreal fire in western Canada and Alaska for the last 300 years except for 1750 and 2000-2008. One possible explanation for mismatch between the fire event and PDO in 1750 and 200-2008 is that the large forest fires in those years may have occurred in western Canada (i.e. British Columbia), where is out of PDO influence. Macias Fauria and Johnson (2008) reported that migration of moist and warm Pacific air to west of the Canadian Rocky Mountains prevents large fire and BB patterns in British Columbia are in anti-phase with those patterns in eastern part of the Rocky Mountains (Macias Fauria and Johnson, 2008, 2006). Another reason is fire may occurred in Alaska during the mismatched years, where PDO has no influence on fire.

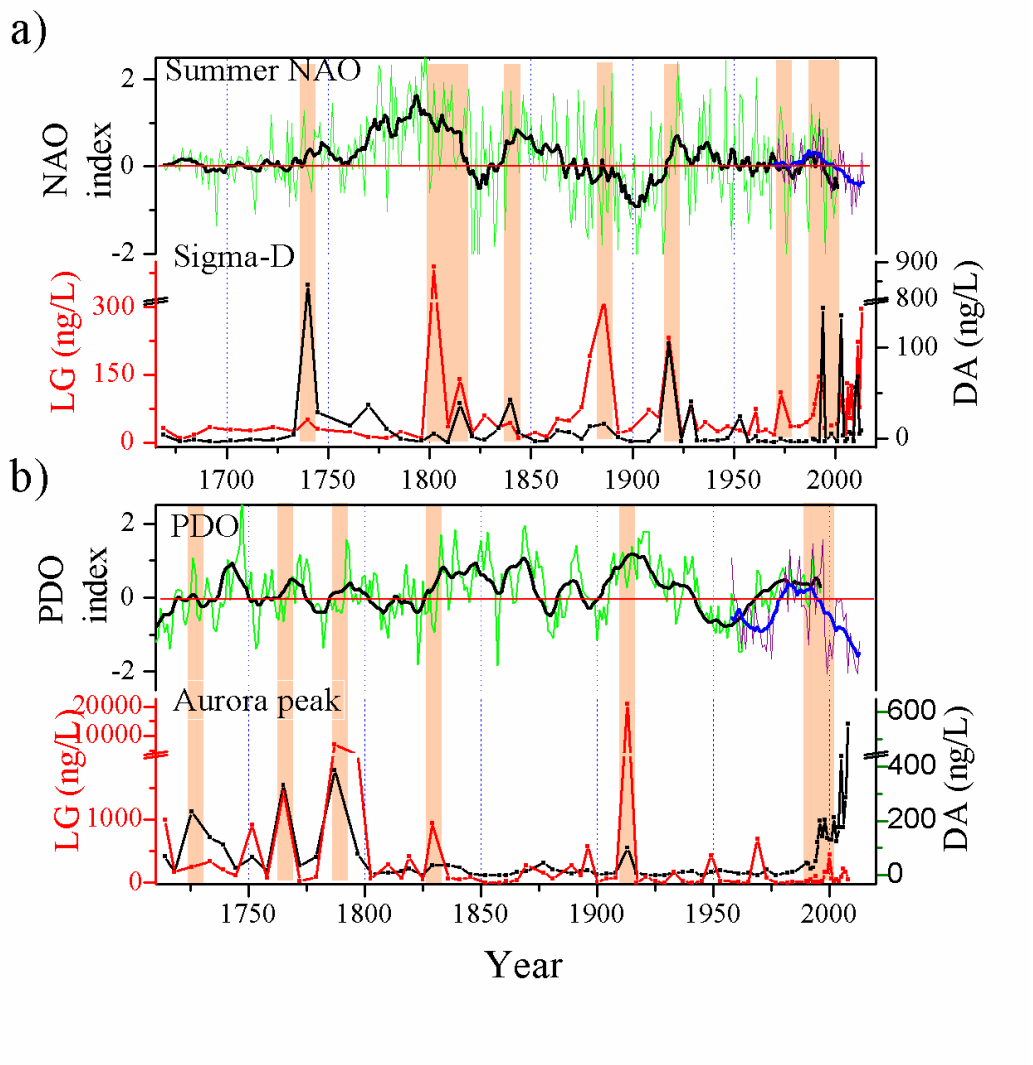

Figure 4.6: Comparisons of BB tracers in the ice core with the reconstructed climatic oscillation for the same time interval. a) Comparison of LG and DA records in Sigma-D ice core with reconstructed summer NAO (Luterbacher, 2001). b) Comparison of LG and DA records in Aurora peak ice core with reconstructed summer PDO record (MacDonald, 2005). The black lines in the PDO and NAO records indicate the 10 years average value. The blue lines represent the instrumental values. The orange shading represents the periods when concentration of BB tracers is high and PDO/NAO were in positive phase.

4.4. Conclusions

This study reported for the first time the historical record of organic BB tracers in Sigma-D and Aurora peak ice cores, which primarily reflect multidecadal variations in the frequency of boreal forest fire in the North America. Fire in the boreal forest was enhanced in Alaska and Western Canada during the LIA. Few sporadic high peaks of the BB tracers have been observed during the industrial revolution era. The ice core record of DA, which is a specific tracers of conifer tree burning showed a gradual increase from 1980s to the present, indicating that fire in boreal coniferous forest has increased over the last 30 years in both of Canada and Alaska. Changes in the concentrations of LG and DA in both of the ice cores coeval with the fluctuations of regional summer temperatures, indicating changes in proximal regions temperature is the major driver for intensifying the boreal forest fire in North America. Furthermore, positive phases of NAO likely exert an influence on fire dynamics in eastern Canadian boreal forest.

Chapter 5

Historical records of organic aerosol loading in Greenland ice core: influences of biomass burning, anthropogenic and biogenic emissions

We reconstructed the primary and secondary organic aerosol (SOA) loading in eastern Canada over the past few hundred years based on organic molecule tracer analyses in Greenland ice core (Sigma-D). Additionally, we reconstructed the abundances of brown carbon (BrC), which heat the atmosphere by absorbing the visible to ultraviolet wavelengths from the ice core. Vanillic acid (VA), which is a lignin pyrolysis product and thus a BB tracer, shows strong correlation with conifer tree burning tracer (dehydroabietic acid), indicating the emission of vanillic acid mainly from boreal coniferous forest fire in eastern Canada over the last few hundred years. Isoprene and monotepene derived SOA tracer records correspond to the BB tracer record, suggesting contribution of BB along with photosynthesis in the emission of biogenic volatile organic carbon and same transport pathways of levoglucosan and SOA tracers to the ice core site. Relatively high abundances of BrC has been found during 1700-1850 compared to the last 150 years. The causes of the variability are complex, depending on atmospheric circulation, changes in emissions, and other factors such as temperature, vegetation changes and wild fire.

5.1. Introduction

Organic aerosols (OA) is thought to influence air quality, biogeochemistry and the climate through interactions with reactive trace gases, water vapor, clouds, precipitation and radiation (Haywood and Boucher, 2000; Ramanathan, 2001). They can influence climate by changing the earth's energy budget by scattering and absorbing the radiation or acting as cloud condensation nuclei (Aalto et al., 2001; Clark et al., 1994; Haywood and Ramaswamy, 1998; Jacobson, 2001). Studying organic aerosols trapped/deposited in the ice of the glaciers can tell us about the information on the aerosol chemical compositions, source regions, as well as, allow us to deduce the influence of aerosol radiative forcing on past climate change. Hence, ice core is a fascinating source of information about the earth's climate; scientists have studied ice samples collected from the different parts of the world for decades to get a glimpse into past changes of atmospheric composition (Fu et al., 2016; Grieman et al., 2016; Kawamura et al., 2012; Kehrwald et al., 2012; Pokhrel et al., 2016; Zennaro et al., 2014).

Organic aerosol consists of two major chemical components: black carbon (BC), which primarily absorbs solar radiation, and organic matter (OM), which scatters as well as absorb solar radiation. The absorbing component of OM, is referred to as brown carbon (BrC) (Andreae and Gelencsér, 2006). It is well established that BC strongly absorb the solar radiation over a broad range of wavelengths, resulting in a direct positive radiative forcing (Bhat et al., 2017; Bond et al., 2013; Ramanathan and Carmichael, 2008). In contrast to BC, BrC, a certain group of organic carbon (OC), can also heat the atmosphere by absorbing the light from the visible (VIS) to ultraviolet

(UV) wavelengths (Andreae and Gelencsér, 2006). BrC potentially exerts on the environment and climate on both global and regional scales.

Terrestrial vegetation emits large quantities (~$PgCy^{-1}$) of biogenic volatile organic compounds (BVOCs), including reactive species such as isoprene and monoterpenes, to the atmosphere (Limbeck, 2003). BVOC emissions undergo rapid oxidation in the atmosphere, generating the climate pollutants such as ozone and biogenic secondary organic aerosol (BSOA) (Adams et al., 2000; Arneth et al., 2009). Moreover, the BVOCs have their primary sink in the troposphere through reaction with hydroxyl (OH) radical, which is also the main sink for methane. Because of this competition for the OH sink, increase in the emissions of BVOCs impacts on lifetimes of the greenhouse gases, i.e. methane (Schurgers et al., 2009) and consequently contribute to warming (Kiendler-Scharr et al., 2009). On the other hand, those SOAs are an important component of earth's atmosphere. It is believed that SOA are more abundant than directly emitted primary organic aerosol (POA) and act as a climate condensation nuclei, influencing local climate (Claeys et al., 2004). Although these organic aerosols (including BrC and BVOC derived SOA) has a large potential to impact on climate, their substantial role and impact is still largely uncertain. A sound knowledge of long-term variability of those aerosols associated with climate change is fundamental to better understanding of substantial role of those aerosols in climate system and provides necessary background for improving predictions of future climate changes.

Past changes in both BB aerosol and SOA can be estimated from tracer analysis in ice core (Ding et al., 2012; Simoneit et al., 1999). Organic tracers are becoming more commonly used as source indicators because they are specific to the sources of

pollutants. In the recent years, BB and SOA tracers have been applied to ice cores to reconstruct variability of those aerosol loadings in past in Russia (Fu et al., 2016; Kawamura et al., 2012), North America (Zennaro et al., 2014) and Alaska (Pokhrel et al., 2016)). However, long-term variability in the BVOC derived aerosol loading in the atmosphere in eastern North America has not been studied yet. Hence, we reconstructed the variability of aerosol loading in the eastern Canada over the few hundred years from Sigma-D ice core. Additionally, we for the first time attempt to reconstruct the variability of BrC based on measuring the light absorbing properties in the ice core.

5.2. Sampling site description

Ice core sample has been collected from the Northwestern part of Greenland (Sigma-D ice core). Detail description of the sampling site and sampling procedure has been given in chapter 4. The methodology of organic aerosol (SOA and BB) tracers and BrC measurement has also been discussed in chapter 2.

5.3. Results and discussion

Table 5.1 presents concentrations of BB and biogenic SOA tracers and abundances of BrC in terms of absorption coefficient in Sigma-D ice core since 1669. We detected three BB tracers in Sigma-D ice core: LG, DA and Vanillic acid (VA). The sources and properties of LG and DA have already been discussed in chapter 3 and 4. Hence, among the BB tracers, the sources of VA only has been discussed in this chapter. As for the biogenic SOA tracers, monoterpene and isoprene derived SOA tracers have been detected in Sigma-D ice core.

Table 5.1: Summery of the BrC, BB and SOA tracers (ng/L) in Sigma-D ice core from Greenland in 1669-2013.

	Concentrations (ng/L)			
	Max	**Min**	**Average**	**Stdev (±)**
BB tracers				
Levoglucosan	348.67	BDL	36.01	70.12
Dehydroabietic acid	887.37	BDL	39.05	108.62
Vanillic acid	1050.00	BDL	24.28	128.51
Monoterpene SOA tracers				
Pinic Acid	238.56	BDL	24.79	51.34
3-HGA	853.44	BDL	83.94	158.60
Isoprene SOA tracers				
2-methylglycericacid	92.37	BDL	9	13.66
C5 alkene triols	171	BDL	12.63	31.97
2-methyl tetrols	411	BDL	43	86.45
Sum of isoprene SOA tracers	606	BDL	63.97	118.97
BrC {a(320nm) (m^{-1})}	0.48	0.01	0.11	0.09

5.3.1. Historical record of vanillic acid (VA)

VA, is produced from the pyrolysis of lignin and they retain the basic structure of the lignin backbone (Legrand et al., 2016; Simoneit, 2002; Simoneit et al., 1999) and thus, has been considered as an BB aerosol tracer. This compound has been studied in BB atmospheric aerosols and in few ice core studies (Grieman et al., 2018, 2016; Haque et al., 2016; Kawamura et al., 2012; Oros and Simoneit, 2000; Simoneit et al., 1999). These studies have shown that burning of conifer and deciduous trees produce VA. The lifetime of this aromatic acid in the gas phase is one to several days in the atmosphere (Donahue et al., 2013). In Sigma-D ice core, the time series of VA concentration is widely consistent with that of DA record (Fig. 5.1a and b). Although VA can emit from

the burning of both deciduous and conifer trees, the strong correlation of VA with the conifer tree burning tracer (DA) ($R=0.97$, $P<0.001$) indicates the emission of VA mainly from the boreal coniferous forest fire in eastern Canada over the last three hundred centuries.

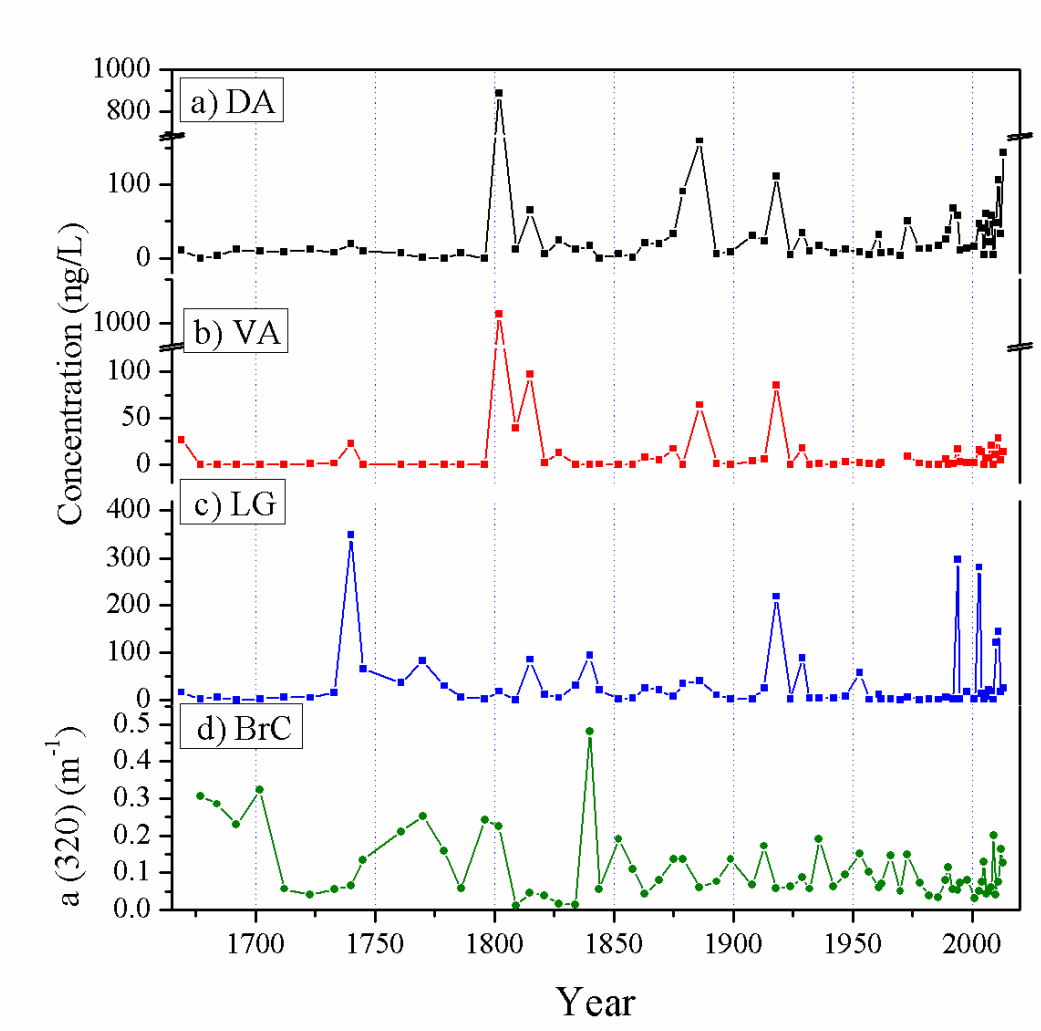

Figure 5.1: Temporal variation of dehydroabietic acid (a), vanillic acid (b), levoglucosan (c) and absorption coefficient (320nm) (brown carbon) (d) in Sigma-D ice core.

5.3.2. Historical records of brown carbon (BrC)

The changes in the abundances of BrC in the last three hundred years are shown in Figure 5.1d, by means of absorption coefficient, as absorption coefficient indicates the abundances of those light absorbing compounds (Yamashita et al., 2013). Although BrC shows considerable fluctuation in abundances over the last few hundred years, relatively high abundances of this organic matter have been found during 1700-1850 compared to over the last 150 years. It has been reported that BrC is emitted from numerous primary sources such as, BB (Saleh et al., 2014; Washenfelder et al., 2015), fossil fuel (e.g., coal) combustion (Yang et al., 2009), biogenic aerosols (e.g., plant debris and fungi) and soil humic substances. Additionally, BrC could also be secondarily formed from anthropogenic or biogenic precursors (Lack et al., 2013; Zhang et al., 2011). Such precursors like isoprene (Limbeck, 2003) and, lignin pyrolysis products (Gelencsér, 2003) could yield BrC through heterogeneous or multiphase reactions in the presence of sulfuric acid or hydroxyl radicals. However, it's difficult to infer that which source is the dominant in eastern Canada over the few hundred years.

5.3.3. Historical records of biogenic SOA tracers

We detected two monoterpene oxidation products in the ice core samples: 3-hydroxyglutaric acid (3-HGA), and pinic acid (Fig. 5.2). Pinic acid is a first-generation products from oxidation of α and β-pinenes, the most abundant monoterpenes, by hydroxyl radical (OH), O_3, or nitrate radical (NO_3) (Hallquist et al., 2009; Ma et al., 2007). Our ice core record of pinic acid shows sporadic peaks in the last three hundred years. Conversely, 3-HGA, which is a higher generation oxidation products of α-pinene

under radiation in the presence of NO_x (Claeys et al., 2007), shows high peaks during 1700-1750, 1800-1850 and 1990 to 2004. Concentration of 3-HGA (av. 84 ng/L) is found to be more abundant than that of pinic acid (av. 25 ng/L) (Table 5.1). However, in Aurora peak and Ushkovsky ice cores, concentrations of 3-HGA are very low compared to that of pinic acid (Fu et al., 2016; Pokhrel et al., 2016).

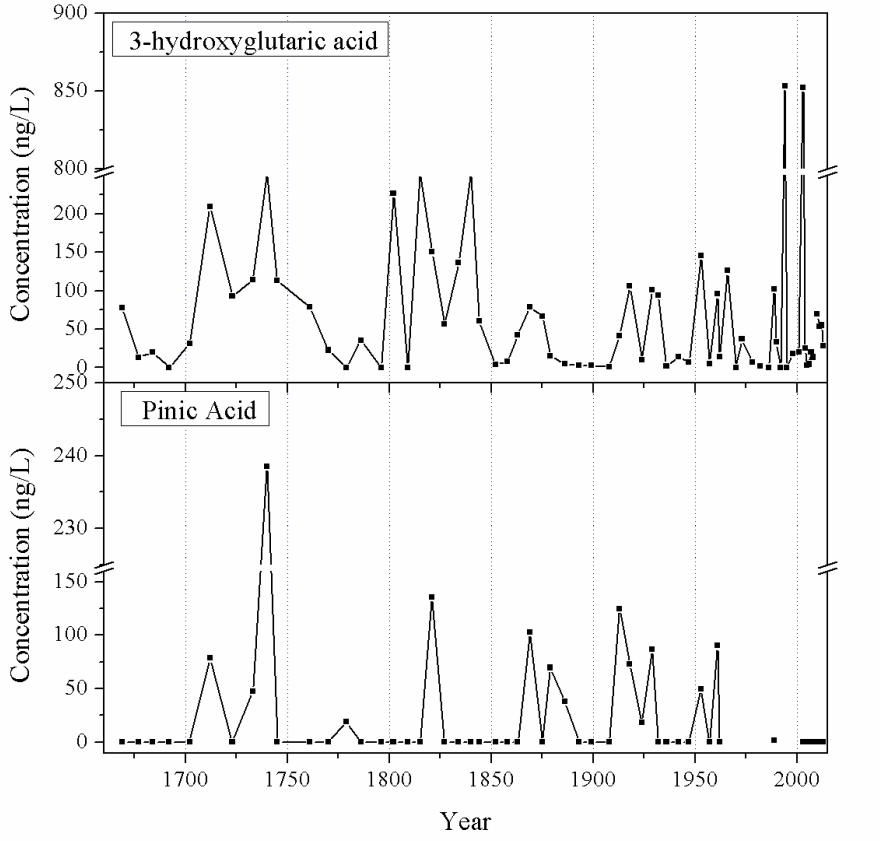

Figure 5.2: Changes in concentrations of monoterpene derived secondary organic aerosol (SOA) tracers in the Sigma-D ice core over the past 350 years.

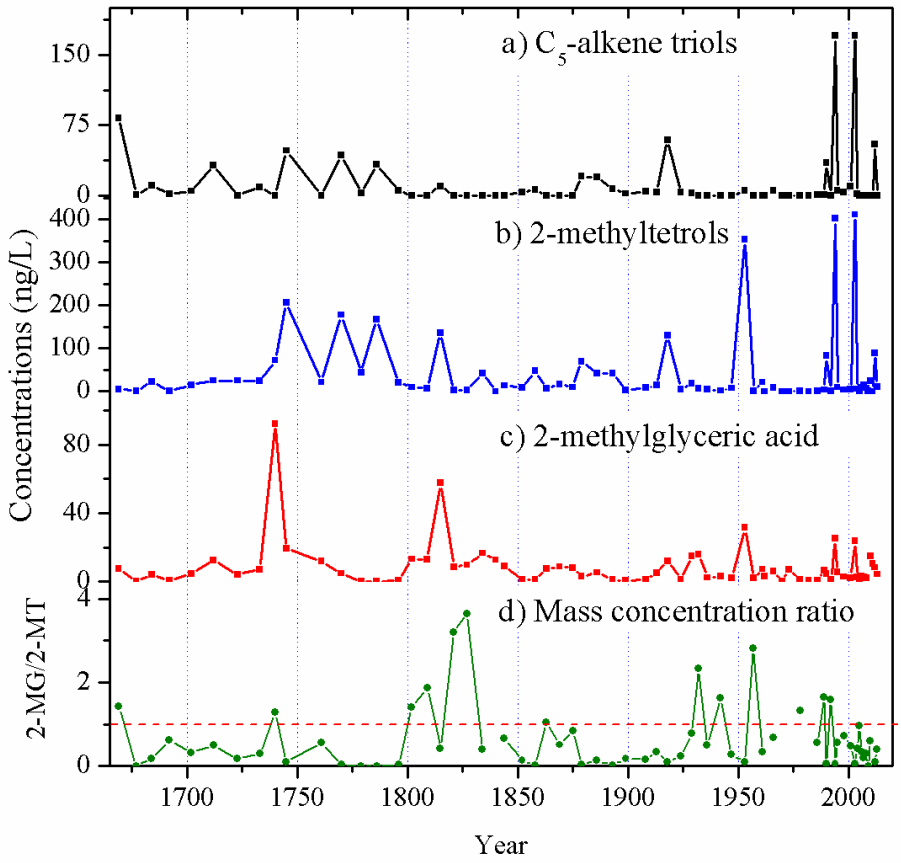

Figure 5.3: Historical trends in the concentrations of isoprene SOA tracers (a-c) and mass concentration ratio (d) in the Sigma-D ice core.

In Sigma-D ice core, three kinds of isoprene derived SOA tracers have been detected (2-methyltetrols (2-MT), C5-alkene triols, 2-methylglyceric acid (2-MGA)). Concentrations of 2-MT, the sum of 2-methylthreitol and 2- methylerythritol ranged from BDL to 411 ng/L (av. 43 ng/L; Table 5.1) in the Sigma-D ice core. 2-MT and C5-alkene triols are higher generation products formed from the photooxidation of epoxydiols of isoprene under low-NOx (NOx = NO + NO2) or NOx-free conditions

(Carlton et al., 2009). Sigma-D ice core 2-MT data shows high peaks during 1740-1820 and the recent few decades. By contrast, 2-MGA, which is a C4-dihydroxycarboxylic acid, has been identified as a key gas-phase intermediate resulting in isoprene SOA formation from the high-NOx pathway (Lin et al., 2013; Nguyen et al., 2015). 2-MGA was found to be less abundant than 2-MT in more than half of the ice core samples (Fig. 5.3d). The ratio of 2-MGA/2-MT varied from 0.00 to 3.65 (mean ratio ~ 0.64) in the last three hundred years. These results suggest that the low-NOx pathway (Carlton et al., 2009) has dominated isoprene photooxidation at the high latitudes in the Northern Hemisphere during the past 350 years.

In general, emission of monoterpene BVOCs through photosynthesis is believed to increase from the conifer trees with abiotic and biotic stresses (Holopainen and Gershenzon, 2010), like, high temperature, high light and herbivore attack. On the other hand, isoprene is mainly emitted from oak forest rather than boreal forest through phosysthesis (Lamanna and Goldstein, 1999). However, it has been reported that isoprene is also emitted from certain conifers such as *Piceaabies*along (Kourtchev et al., 2005). In addition, the isoprene and monoterpene BVOCs are also emitted from leaf litter and marine phytoplankton, although oceanic emissions of BVOC is considered to be very small compared to the global burdens (Guenther et al., 1995., Faiola et al., 2014; Shaw et al., 2003).

The SOA tracers records in Ushkovsky ice core, far east Russia is found to correlate with summer temperature record in China (Fu et al., 2016). Hence, we compare the Sigma-D ice core BSOA tracer records with summer temperature in eastern Canada, as it is the source region of the BSOA deposited in the ice core. However, eastern Canada summer temperature record does not significantly agree with the

monoterpene and isoprene derived SOA tracer records (Fig. 5.4), indicating an importance of other factor for the emission of the BVOCs and their subsequent photo oxidation. Conversely, Sigma-D ice core LG record significantly correlate with isoprene ($R=0.64$-0.71; $p<0.001$) and monoterpene derived SOA tracers ($r=0.59$ to 0.79, $p<0.01$) (Table 5.2). This empirical correlation suggests that vegetation fire is also important source of isoprene and monoterpene emission along with plant photosynthesis and similar transport pathway of those tracers (BB and BSOA) to the ice core site. It is noteworthy that recent studies also inferred the BVOC emission from vegetation fires (Fu et al., 2016; Haque et al., 2016).

Table 5.2: Correlations of ice core Biogenic SOA tracers and levoglucosan record.

Biogenic SOA tracers	**Correlation coefficient with levoglucosan**	**P value**
Monoterpene derived SOA tracers		
Pinic Acid	0.56	<0.001
3-HGA	0.79	<0.001
Isoprene derived SOA tracers		
2-methylglyceric acid	0.71	<0.001
C5 alkene triol	0.61	<0.001
2-methyl tetrols	0.64	<0.001
Sum of isoprene SOA tracers	0.71	<0.001

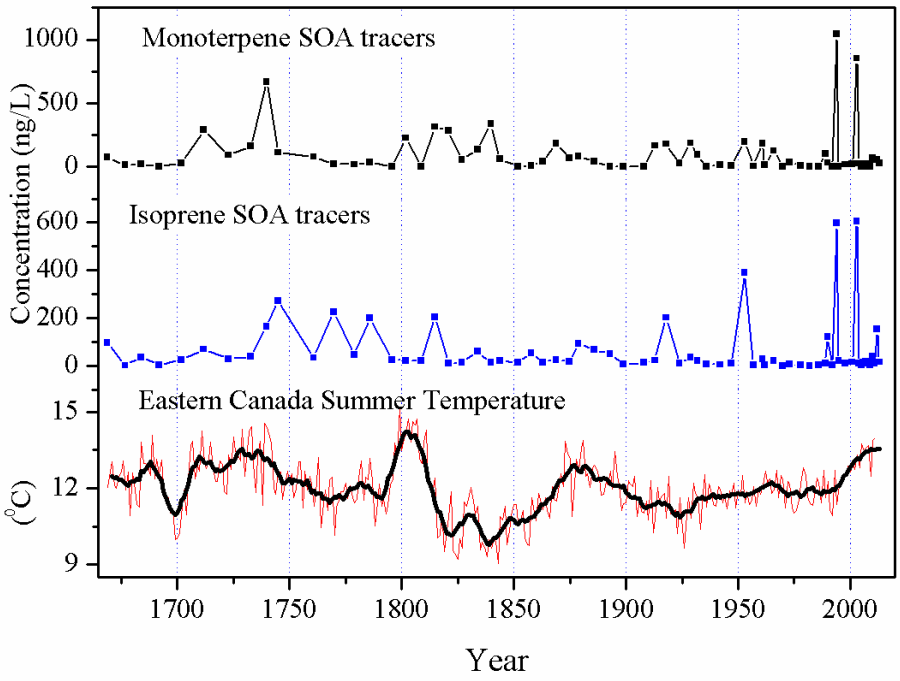

Figure 5.4: Comparison of sum of the isoprene SOA tracers (a) and monoterpene SOA tracers (b) with summer temperature record in Eastern Canada (c) (Gennaretti et al., 2014). The black lines in the temperature records represent10 years average value.

5.4. Conclusions

Long-term changes in emissions of BB, BVOC derived-SOA tracers and BrC in eastern Canada has been reconstructed from Sigma-D ice core, Greenland. We found positive correlations of VA and DA, which is conifer tree burning tracers, indicating the emission of VA from coniferous forest fire and same transport pathways of VA and DA to the ice core site. The concentrations of isoprene and monoterpene derived SOA tracers in Sigma-D ice core are relatively high in the 18th centuries and the recent decades. The isoprene and monoterpene derived SOA data are found to resemble with that of LG record. This result suggests plant burning plays an important role in emission of the BVOC. BrC, the light absorbing organic carbon record in Sigma-D ice core shows relatively high abundances during 1700-1850 compared to the last 150 years in the ice core.

Chapter 6

Thesis Conclusions

We for the first time assessed the paleoclimatic utility of the BB tracers (LG and DA) using well-dated ice core (SE-Dome) in Greenland. Furthermore, we for the first time reconstructed the boreal forest fire history in North America over the past few hundred years from LG and DA records in the two ice cores in Greenland and Alaska to investigate causal link between boreal forest fire and climate.

We generated continuous records of BB molecular tracers over the last 60 years from SE-Dome ice core to assess applicability of BB molecular tracers in the ice core. A comparison of our ice core tracer records with those of other ice cores indicates that concentrations of BB tracers in ice cores likely reflect differences in the BB magnitude in the source area and the snow accumulation rate. LG and DA data in the SE-Dome ice core record most of the BB events in eastern Canada from 1958 to 2014. However, the BB events in western Canada are not recorded in SE-Dome ice core. Ice core analyses of LG and DA in Greenland ice cores are a promising approach to reconstruct the BB frequency in eastern Canada.

Furthermore, we reconstructed boreal forest fire history in North America from analyses of organic BB tracers in Sigma-D and Aurora peak ice core. Fire in the boreal forest was enhanced in the LIA, especially in Alaska and western Canada. Few prominent BB events have been observed during the industrial revolution era. Fire in boreal coniferous forest has increased over the last 30 years in both part of Canada and Alaska. Climate warming is the major driver for intensification of the forest fire in North America. Furthermore, NAO exert an indirect influence on fire dynamics in

eastern part of Canada with reducing the precipitation intensity and increasing lightning induced fire during the positive phases. Hence, we concluded that several climatic factors are combined to generate favorable conditions for large wildfire in the last few hundred years.

Furthermore, we provide long term records of BVOC-derived SOA tracers and BrC in Sigma-D ice core, Greenland over the past 350 years. Our results show the increase in emission of the BVOCs during BB along with photosynthesis. Sigma-D ice core record of BrC, which is also contribute to warming, shows relatively high abundances during 1700-1850 compared to the last 150 years. Our study highlights the previously unexploited potential of organic aerosol tracers in ice core for paleoclimatic applications.

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