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Molecular compositions and seasonal variations of organic compounds in atmospheric aerosols from subarctic Alaska

亜北極アラスカにおける大気エアロゾル中の有機化合物組成と季節変動

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Abstract

Organic constituents are recently highlighted because they account for a substantial portion of atmospheric particles, up to 50% in mass. Global models predict that biomass burning emissions and secondary organic aerosols (SOA) formation from biogenic volatile organic compounds (BVOCs) are the two major sources of organic aerosols (OA). Most of them are water-soluble and they can act as cloud condensation nuclei and ice nuclei, affecting climate by altering the hygroscopic properties of aerosols. Total of 32 total suspended particle (TSP) samples were collected from Fairbanks, Alaska in June 2008 to June 2009 using a low volume air sampler at a flow rate of 16.7 L/min. Here, we report the molecular compositions and seasonal variations of anhydro-sugars (levoglucosan, galactosan and mannosan), lignin & resin acids (4-hydroxybenzoic, syringic, vanillic and dehydroabietic acids) and biogenic SOA tracers (isoprene, α-/β-pinene and β-caryophyllene SOA tracers) which were measured using solvent extraction/TMS-derivatization technique followed by gas chromatography-mass spectrometry (GC-MS) determination.

Anhydro-sugars and lignin & resin acids are specific tracers from biomass burning emissions. Levoglucosan was observed as a dominant biomass burning tracer (average 66.8 ng m^{-3}) followed by its two isomers: mannosan (15.0 ng m^{-3}) and galactosan (ave. 9.88 ng m^{-3}). All anhydro-sugars showed similar temporal and seasonal trends with high abundant in winter and autumn. All lignin and resin products exhibited similar temporal and seasonal variations with levoglucosan in winter maximum and spring minimum. Dehydroabietic acid was detected as a most abundant (ave. 8.51 ng m^{-3}) tracer among all lignin and resin products. The analyses of air mass back trajectories and fire spots demonstrated that biomass burning tracers may be associated from residential heating and cooking in regional area, especially in cold season. Levoglucosan contributed 2.92% to WSOC and 1.62% to OC. The highest

values of WSOC (6.26%) and OC (3.63%) in winter time indicate that contribution of biomass burning to Alaskan aerosols is important in winter period.

The concentration level of isoprene oxidation products was higher (ave. 4.14 ng m^{-3}) than α-/β-pinene- (2.01 ng m^{-3}) and β-caryophyllene-SOA product (1.53 ng m^{-3}). Isoprene-SOA tracers showed higher concentrations in summer (ave. 8.77 ng m^{-3}), whereas α-/β-pinene- and β-caryophyllene-SOA tracers exhibited highest levels in spring (3.55 ng m^{-3}) and winter (4.04 ng m^{-3}), respectively. β-Caryophyllinic acid and levoglucosan showed a positive correlation, indicating that biomass burning may be a major source for β-caryophyllene. Using a tracer-based method, the amount of secondary organic carbon (SOC) were estimated for isoprene (ave. 159 ngC m^{-3}), α-/β-pinene (35 ngC m^{-3}) and β-caryophyllene (66.3 ngC m^{-3}). Based on SOA tracers, this study suggests that isoprene is a more important precursor for the production of biogenic SOA than α-/β-pinene and β-caryophyllene in subarctic Alaska.

All primary sugars and sugar alcohols except xylose and erythritol showed higher concentrations in summer and spring than winter and autumn due to the abundance of vegetations, pollens and developing flower buds in spring/summer period in Alaska region. Sucrose was most dominated tracer (30.5 ng m^{-3}) among all the primary sugars and sugar alcohols. Positive linear correlation between nss-Ca^{2+} and arabitol indicates that sugar alcohols partly derived from soil microbes. On the other hand, xylose and erythritol exhibited higher concentrations in winter and lower in spring, which is similar with those of levoglucosan, indicating that they are originated from biomass burning. Based on air masses backward trajectories, it can be predicted that primary biological aerosol particle (PBAPs) tracers mainly derived from regional boreal and tundra forest or local vegetations due to the high biological activities in spring and summer period.

The present study demonstrated clear seasonal trends for biomass burning tracers with high abundance in winter/autumn, whereas biogenic SOA tracers, primary sugars and sugar

alcohols were dominated in summer/spring. In this study, mixed air masses origin were observed in all seasons when air masses mainly come with short distance over Oceanic regions and some of from Alaska regional area to sampling place. This result suggests that regional emission is the important source for organic aerosols in Alaska atmosphere. Positive matrix factorization (PMF) analysis demonstrated that biomass burning is the important source (49.2%) in Alaska aerosols. Based on forward trajectories from sampling area, it should be proposed that Alaska pollutants can be transported to the Arctic which can affect the Arctic climate. Thus, the current study will be useful to better understand the effect of organic aerosols on Arctic or subarctic atmosphere.

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Chapter 1: Introduction

1.1. Aerosols in the atmosphere

Aerosol is a term of colloidal system where solid or liquid particles are dispersed in a gaseous phase. Aerosols can be found in the air over oceans, deserts, mountains, forests, ice, and every ecosystem in between. Atmospheric aerosols are generally considered as particles having range size in diameter from a few nanometers (nm) to 10 micrometer (μm) (Fig. 1). Despite their small size, they have major impacts on our climate and our health. Different specialists define the particles based on shape, size, and chemical composition. Toxicologists introduce to aerosols as ultrafine, fine, or coarse matter. Regulatory agencies and meteorologists, refer them particulate matter—$PM_{2.5}$ or PM_{10}, depending on their size. Climatologists typically call them chemical composition as well as key aerosol groups include sulfates, organic carbon, black carbon, nitrates, mineral dust, and sea salt. All characterizations are imperfect in terms of their field, as aerosols often clump together to form complex mixtures. Particulate matter in the lower atmosphere (troposphere) is composed of highly water soluble inorganic salts, insoluble mineral dust and carbonaceous components [*Jacobson et al.*, 2000].

Aerosols can be natural or artificial. The natural aerosols are fog, forest exudates and geyser steam, where as artificial aerosols are haze, dust, particulate air pollutants and smoke. Primary aerosols contain particles that directly emit into the atmosphere and secondary aerosols form through gas-to-particle conversion. Hence, aerosols remain suspended in the atmosphere for short periods, typically between few days and a week—they can travel vast distances with the air current. Particles moving with the atmosphere at 5 meters/ second will travel thousands of kilometers in a week. During transportation aerosol can be oxidized. However, the lifetime of aerosols in the atmosphere is still not clear understood. The lifetime of aerosols typically depends on aerosols properties and meteorological conditions. Aerosols

can be removed from the atmosphere by wet or dry deposition process due to gravitational force.

1.2. Atmospheric effect of aerosols

Aerosols are believed to have important impacts on climate and human health, although the magnitudes of these impacts remain quite uncertain. However, their impacts on climate are very complex and difficult to quantify [*Koch et al.*, 2007]. Atmospheric aerosols have direct effect on Earth's radiation field by scatter or absorb sunlight (Fig. 2). The scattering or absorbing characteristic of aerosols depends on their physical properties, which can modify the radiative balace of the atmosphere (*IPCC*, 2007). Although most aerosols reflect sunlight, some also absorb that depends primarily on the composition and color of the particles. It was established that atmospheric aerosol play an important role to reduce visibility [Horvath, 1993], and cause acidification and eutrophication of ecosystem [*UNECE*, 2004]. Pure sulfates and nitrates reflect almost all radiation they encounter, cooling the atmosphere. In contrast, black carbon absorbs radiation readily, warming the atmosphere but also shading the surface. Brown carbon or organic matter, has a warming influence on the atmosphere depending on the brightness of the underlying ground.

Although aerosols can influence climate by scattering light and changing Earth's reflectivity, indirectly they can also alter the climate via clouds (Fig 3). Aerosols play a critical role to the formation of cloud which interacts with radiation [*Silvergren et al.*, 2014]. The prediction of future climate for various scenarios has large uncertainty and the majority of this uncertainty stems from lacking of knowledge concerning aerosols and in particular from aerosol-cloud interactions [*Forster et al.*, 2007]. Aerosol type plays an important role in determining the affect clouds by aerosols. The reflective aerosols tend to brighten clouds and make them last longer, where as the black carbon from soot can have the opposite effect. The smaller droplets reduce the precipitation efficiency and enhance the cloud life time and hence

the cloud reflectivity (*Albrecht*, 1989). Absorption of solar radiation by aerosols leads to heating of the air, which can imply in an evaporation of cloud droplets. Natural aerosols such as sulfates, sea salt or ammonium salts—are the most common condensation nuclei in pristine environments. Usually polluted air contains much higher concentrations of water-soluble particles, which indicats pollution-rich clouds tend to have more numerous, but smaller, droplets. Previous studies reported that the production of sulphate in cloud drops can contribute significantly to the aerosol mass [*Hegg et al*., 1996; *Zhang et al*., 1999) and may play role either to an enhancement or to a suppression of the cloud drop number concentration [*Feingold and Kreidenweis*, 2000].

1.3. Sources of aerosols in the atmosphere

There are two possible sources for aerosols particle into the atmosphere. Firstly, particles can directly emit to the atmosphere from various sources such as soil dust, industrial emission, biomass burning, biogenic emission, and sea spray from the Ocean, etc. (Fig. 4). Secondly, particles can be formed through gas-to-particle conversion, heterogeneous reactions, etc. The major part of atmospheric aerosols around 90% by mass—has natural origins. Volcanoes, one of the examples of natural sources, emit huge amounts of ash into the air, as well as sulfur dioxide and other gases, yielding sulfates. Wild fire produce large amount of aerosols, predominantly in the form of carbonaceous aerosols, namely black carbon (BC) and organic aerosols (OA) [*Kondo et al*., 2011]. Vegetation release huge amount of volatile organic compounds (VOCs) which can be further photo-oxidized to produce secondary organic aerosol [*Ding et al*., 2013].

Sea salt and dust are other abundant aerosols in the atmosphere. Deserts and sandy lands in the northwest and north parts of China and the south part of Mongolia are the main source area of Asia dust storm [*Huebert et al*., 2003; IPCC, 2007; *Zhang et al*., 2003]. Recently satellite observed that the Asia dust was transported more than one full circle around the

world within two weeks [*Uno et al.*, 2009]. It has been known for many years that primary sea spray particles and sulphate, further formed from the oxidation of dimethylsulphide (DMS), are two major component of marine aerosols [*Fu et al.*, 2011]. Fossil fuel combustion and motor vehicles also produces large amounts of sulfur dioxide, which reacts with water vapor and other gases in the atmosphere to create sulfate aerosols.

1.4. Organic aerosols in the atmosphere

Organic constituents are recently highlighted because they account for a substantial portion of atmospheric particles, up to 50% in mass [*Seinfeld and Pandis*, 1998] in the atmosphere. Organic aerosols, which contribute a large fraction (20-90%) of fine aerosols, are released from various primary sources and secondarily produced in the atmosphere by oxidation of VOCs followed by condensation on existing particles and/or nucleation process. A number of studies have reported that organic aerosol plays an important role in both the direct as well as the indirect aerosol forcing [*Cooke et al.*, 1999; *Hansen et al.*, 1998; *Penner et al.*, 1998; *Lohmann et al.*, 2000; *Jacobson*, 2001; *Chung and Seinfeld*, 2002). The polar organic components in the atmosphere can uptake water, which have hygroscopic behavior, can act as a cloud condensation nuclei and ice nuclei [*Albrecht,* 1989; *Ramanathan et al.*,, 2001].

Primary organic aerosols (POA) directly emitted from several sources such as plant material, soil dust, biomass and fossil fuel burning, agricultural waste, etc. There are a number of other types of primary carbonaceous material in the atmosphere such as viruses, bacteria, fungal spores and plant debris [*Bauer et al.*, 2002] that may effective ice nuclei and can form bio-aerosols. Recently a significant marine POA source has been identified in North Atlantic [*O'Dowd et al.*, 2004]. During the period of high biological activity such as phytoplankton blooms, progressing from spring through autumn, bubble bursting produces submicrometre particles enriched in insoluble and high molecular mass organic matter

[*Kanakidou et al*., 2005]. In contrast, secondary organic aerosols produced by the oxidation of gas-phase precursors in the atmosphere. Various types of VOCs are emitted into the atmosphere from natural sources in marine and terrestrial environments, as well as from anthropogenic sources. These volatile components can be further photo-oxidized by OH, NOx etc. to form secondary organic aerosol (SOA) in the atmosphere. Both of the primary carbonaceous aerosol and SOA can contribute to the chemical formation of organic particulate matter in the atmosphere. These organics potentially control the physicochemical properties of atmospheric particles [*Kanakidou et al.,* 2005].

1.4.1. Climatic impact of organic aerosol

Organic aerosols (OA) affect the earth's radiation balance and global air quality. According to large scale model simulations, the direct and indirect radiative effects of the biogenic secondary organic aerosols (BSOA) are significant, yet poorly quantified [*Goto et al* 2008, *Rap et al*., 2013, *Scott et al*., 2014]. Based on the model study, it has been considered that black carbon (BC) to be a climate-warming agent and organic matter (OM) to be a cooling agent. The combined climatic effect of BC and OM can balance radiative force. Organic aerosols play a key role in cloud nucleation process. Model simulation results proposed that organic aerosol can enhance the cloud droplet concentration and act an important component of the Aerosol-cloud-climate feedback system [*O'Dowd et al*., 2004]. Particularly, water-soluble organic carbon (WSOC) influence the hygroscopic properties of aerosol particles and increases their cloud condensation nuclei (CCN) activity [*Asa-Awuku et al*., 2011]. Enhanced CCN number concentrations in the atmosphere might be increased the indirect radiative forcing by aerosol, resulting a more reflective cloud [*Twomey*, 1977] and less precipitation [*Albrecht,* 1989]. The organic aerosol components uptake water and their interactions with the inorganic salts dissolved in the same aqueous phase, directly changes the aerosol water concentration and indirectly aerosol properties [*Kanakidou et al*., 2005].

1.5. Importance of Alaska aerosols

Alaska, one of the biggest states of USA which is bordered by Canada, Arctic Ocean, Bering Sea, and Pacific Ocean. Alaska is located in Arctic and subarctic region where boreal and tundra forests are available. Significant changes in Alaskan climate have occurred during the 20th century, especially some regions changes are observed dramatically through mountain glacier recession, extended growing season length and thawing of permafrost [*L'Heureux et al.*, 2004]. Boreal forest fires are one of the most important sources of aerosols transported to the Arctic [*Stohl et al.*, 2006, 2007; *Treffeisen et al.*, 2007; *Eck et al.*, 2009] and large amounts of carbonaceous aerosols such as black carbon (BC) and organic aerosols (OA), are emitted during burning period. Alaska boreal fires have been recorded for 50 years to show an increasing trend of fire occurrence and area burned [*French et al.*, 2002].

Countries bordering the Arctic – i.e., the Scandinavian countries, Canada, USA and Russia – are well known to use huge amounts of wood for residential heating, which can also release substantial amount of biomass burning tracers in the atmosphere [*Yttri et al.*, 2014]. These biomass burning may have significant impacts on regional direct radiative forcing and also may be transported deep into Arctic regions. Due to the long day length, large path length transmission through the aerosol layers and high underlying surface albedo of ice and snow, the aerosol direct radiative effects can be enhanced at polar latitudes [*Eck et al.*, 2009]. Recent studies demonstrated that a complex relationship exists between climate and tree growth in Alaska [*Barber et al*, 2004; *Lloyd and Fastie*, 2002].

1.6. Purpose of this study

Alaska biomass is an important source of aerosols that can be transported to the Arctic. Large amount of aerosols particle such as carbonaceous components (BC, OC) and inorganic species may be associated with biomass burning. These particles typically absorb and scatter solar visible radiation, affecting the radiation budget in the Arctic, can also act as cloud

condensation nuclei which influence the microphysical properties of clouds [*Kondo et al.*, 2011]. *Kim et al.*, [2005] reported black carbon (BC) effect to the Arctic Sea ice and Alaska glaciers from Alaska boreal wildfire. There are several studies on Alaska aerosols influenced by biomass burning, reported on emission of carbonaceous and inorganic species [*Kondo et al.*, 2011], aerosol optical properties [*Eck et al.,* 2009], carbon and hydrogen stable isotopic ratios of methane [*Umezawa et al.*, 2011], carbon based trace gases from fire plumes [*French et al.*, 2002; *Goode et al.*, 2000]. However, there is no study about the composition and seasonal variations of organic compounds on Alaska aerosols.

The objective of this study is to identification, molecular compositions, and seasonal variations of organic compounds such as biomass burning tracers, primary sugars, sugar alcohols and biogenic secondary organic aerosol tracers from subarctic Alaska. Here, we discussed the possible source of organic components based on fire spots and air mass back trajectories as well as contribution to the Arctic and sub-arctic region using air mass forward trajectories. Contributions of biomass burning and SOA tracers to organic carbon (OC), water-soluble organic carbon (WSOC) and secondary organic carbon (SOC) are also evaluated in the ambient aerosols from subarctic Alaska. The current study presents for the first time one-year observation on biogenic SOA tracers in the subarctic region.

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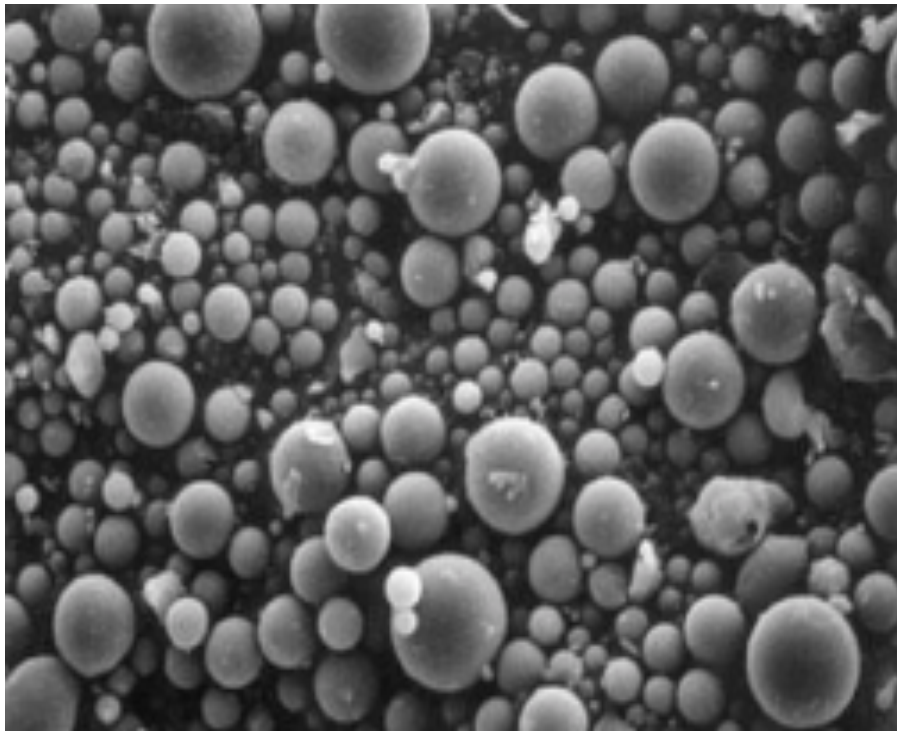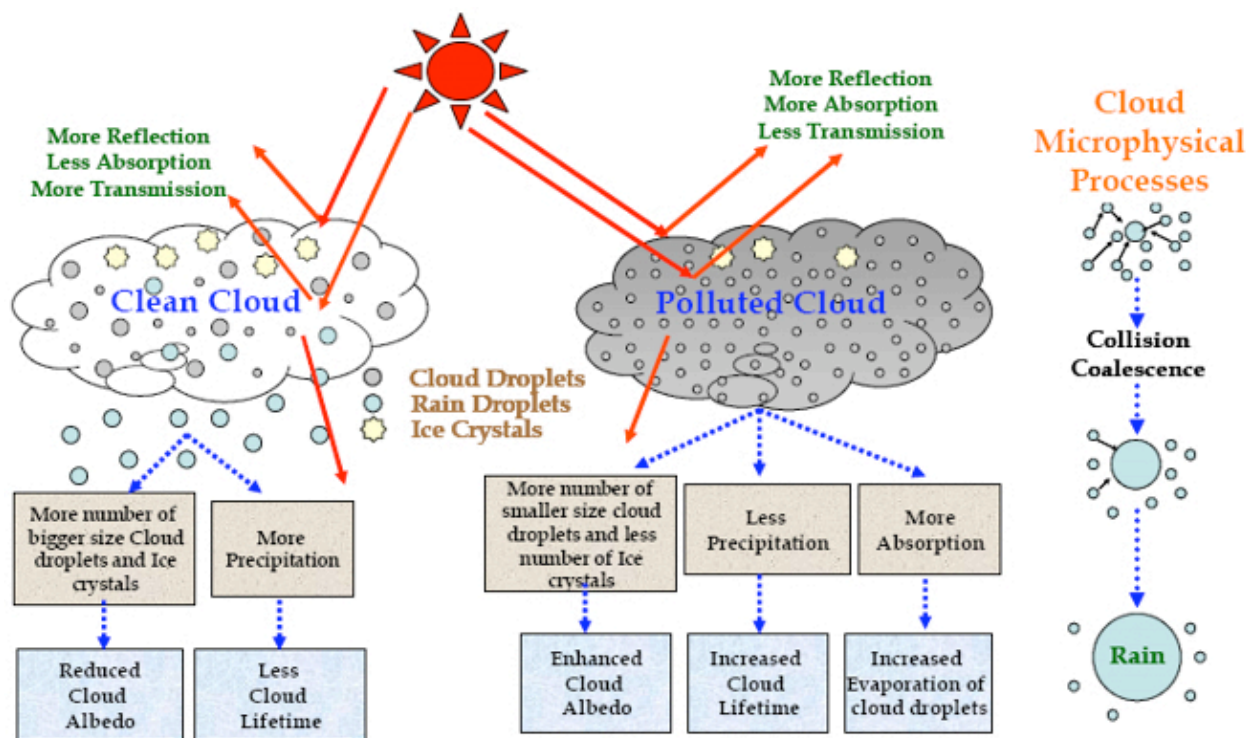
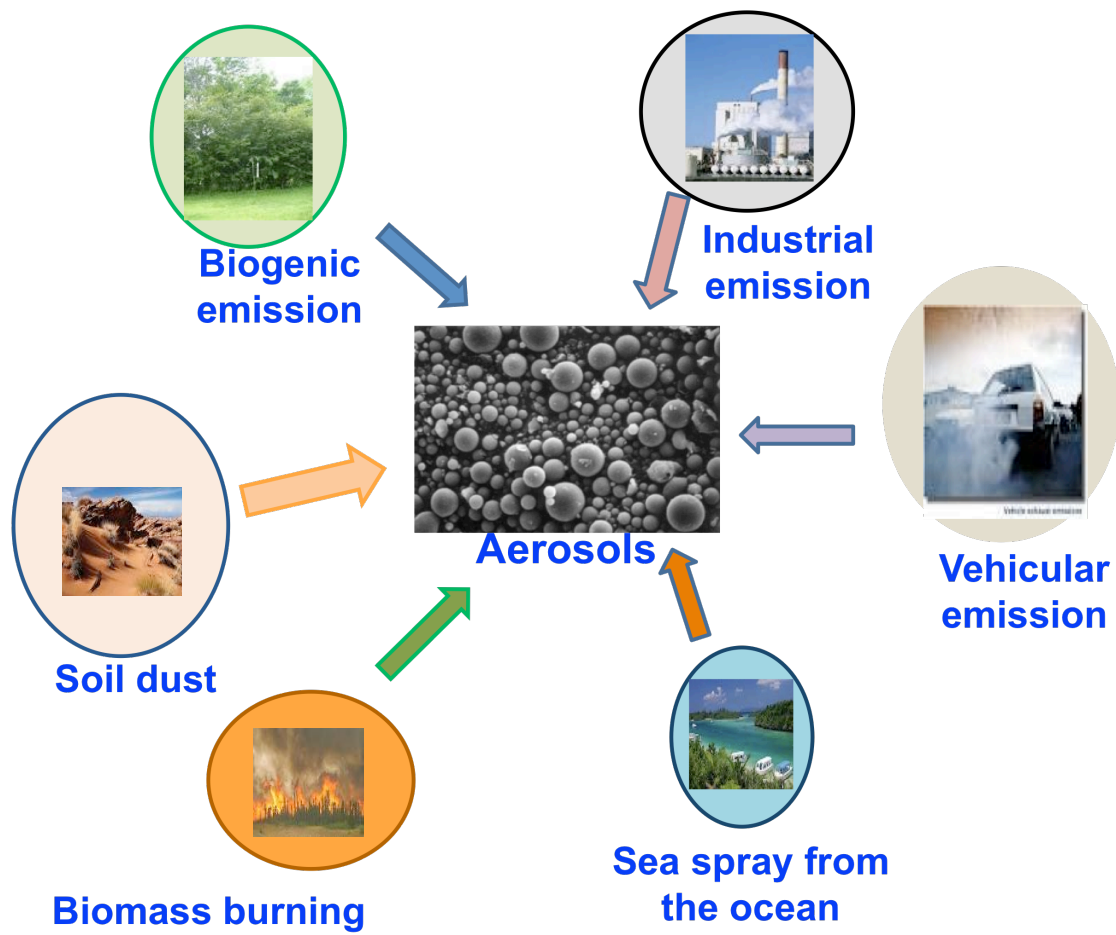**Fig.1**. Photomicrograph of aerosols made with a Scanning Electron Microsope.
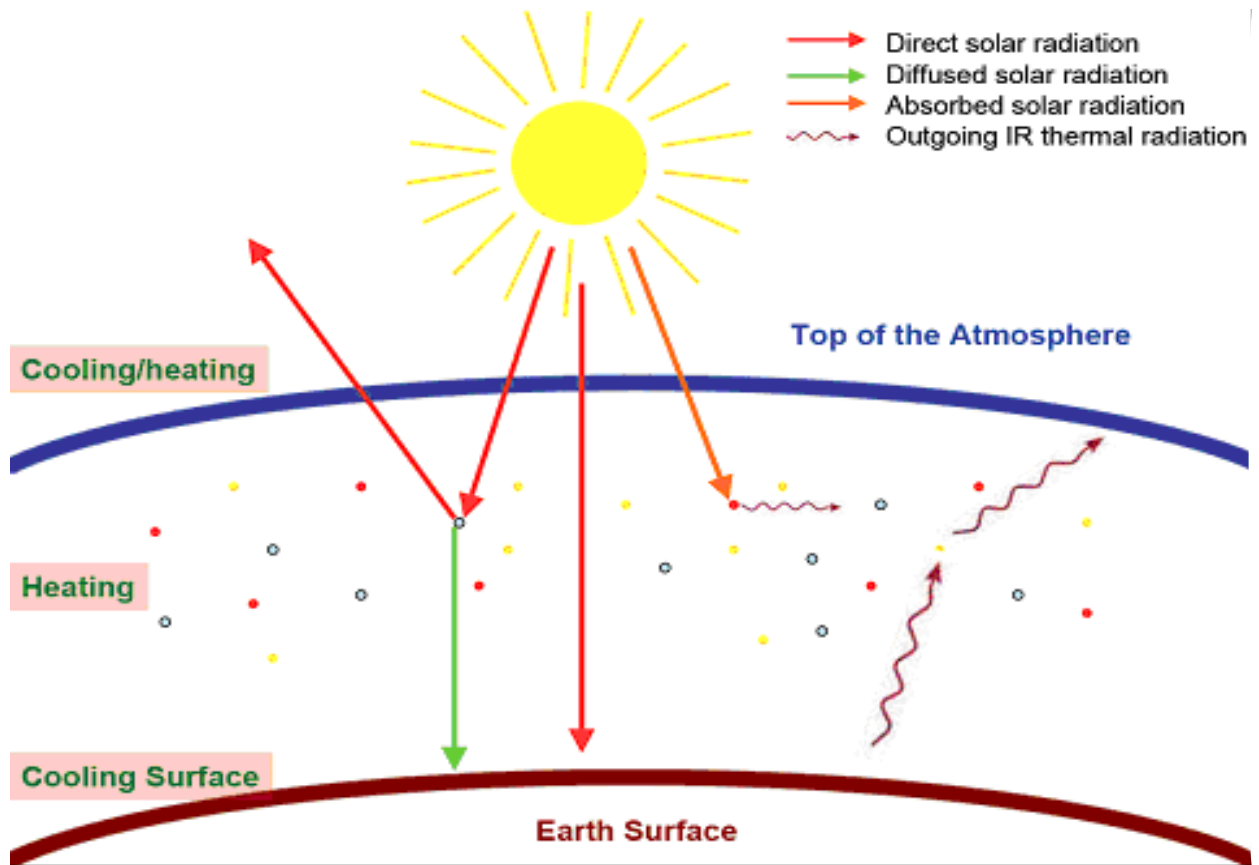
Fig.2. Direct effects of aerosols in the atmosphere

Fig.3. Indirect effects of aerosols in the atmosphere

Fig. 4. Primary sourcers of aerosols in the atmosphere.

Chapter 2. Materials and Method

2.1. Aerosol Sampling

Total suspended particles (TSP, n=32) samples were collected on the campus of the University of Alaska Fairbanks (UAF) (64°51'N; 147°51'W), Alaska USA during June 2008 - June 2009. The University campus is located in down town of Fairbanks where natural forest is very near. A low volume air sampler (NIER) was set up on the rooftop of the International Arctic Research Centre (IARC), UAF. The altitude of sampling point (IARC) is 192 meter above the sea level. Sampling was conducted roughly every one week to three weeks onto pre-combusted (450°C for 6 h) quartz fiber filters (47 mm, HEPA, Pall Corporation, USA) at a flow rate of 16.7 L/min. After sampling, the sample filter was placed in a pre-combusted glass vial (50 mL) with a Teflon-lined screw cap, transported to the laboratory and stored in a dark freezer room at -20°C until the analysis. Figure 1 shows the location of the sampling site and the surrounding area.

2.2. Extraction and Derivatization

Filter aliquots (disk diameter of 20 mm) were extracted three times with 7 mL of dichloromethane/methanol (2:1; v/v) under ultra sonication. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette to remove all insoluble filter debris, concentrated using rotary evaporator under vacuum and then blown down to dryness with pure nitrogen gas. The extracts were then derivatized with 50 μL of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10 μL of pyridine at 70°C for 3h to derive trimethylsilyl derivatives of carboxylic acids, alcohols and sugars, etc. During this procedure, COOH and OH groups are derivatized to the corresponding trimethylsilyl (TMS) esters and ethers, respectively [*Schauer et al.*, 1996; *Simoneit et al.*, 2004b; *Simoneit et al.*, 2004c; *Wang and Kawamura*, 2005]. After the

reaction, the derivatives were diluted with 40 µL of *n*-hexane containing the internal standard (C_{13} *n*-alkane, 1.43 ng/uL) prior to determination by gas chromatography/mass spectrometry (GC/MS).

2.3. Gas Chromatography-Mass Spectrometry (GC/MS)

Gas chromatography-mass spectrometry (GC-MS) analyses of the derivatized total extracts were conducted on a Hewlett-Packard model 6890 GC coupled to Hewlett-Packard model 5973 mass-selective detector (MSD). The GC separation was performed on a DB-5MS fused silica capillary column (30 m x 0.25 mm i.d., 0.5 µm film thickness) with a GC oven temperature program: temperature hold at $50^{\circ}C$ for 2 min then increase from 50 to $120^{\circ}C$ at a rate of $30^{\circ}C$ min^{-1}, further increase from 120 to $300^{\circ}C$ at a rate of $6^{\circ}C$ min^{-1} with a final isotherm hold at $300^{\circ}C$ for 16 min. The sample was injected on a splitless mode with the injector temperature at $280^{\circ}C$. The mass spectrometer was operated at 70 eV and scanned from 50 to 650 Da on the electron impact (EI) mode. Mass spectral data were acquired and processed with the chemstation software. The compounds were identified individually by comparing with respective mass spectra of literature and library data as well as authentic standards and by interpretation of mass fragmentation patterns. GC-MS response factors of individual compound were determined using authentic standards and surrogate compounds.

2.4. Analysis for Organic and Elemental Carbon (OC/EC)

Organic carbon (OC) and elemental carbon (EC) were measured using a Sunset Laboratory carbon analyzer following Interagency Monitoring Protected Visual Environments (IMPROVE) thermal/optical evolution protocol and assuming carbonate carbon in the sample to be negligible [*Wang et al.*, 2005]. An aliquot of quartz filter samples (φ 14 mm) were punched and put in a quartz tube inside the thermal desorption chamber of the analyzer and then combusted with stepwise heating in a helium flow at first and then after

the initial ramp, helium gas was switched to He/O_2. During the oxidation process at each temperature step, the evolved CO_2 was measured with non-dispersive infrared (NDIR) detector system. The transmittance of light at 660 nm through the filter punch was used for setting up OC/EC split point and thereby OC correction. Duplicate analysis of filter samples showed uncertainties within 7% for OC and 5% for EC. The reported concentrations of OC and EC were corrected for the field blanks.

2.5. Analysis of Water-Soluble Organic Carbon (WSOC)

To determine the WSOC concentration, the filter aliquot (φ 18 mm) was extracted with 15 mL of organic free pure water by ultrasonication for 30 min and then filtered with syringe filter (Millex-GV with 0.22 µm pore size, Millipore). Finally the WSOC in water extracts was measured using a total organic carbon (TOC) analyzer (Model TOC-Vcsh, Shimadzu, Kyoto, Japan) (*Miyazaki et al*., 2011). The concentrations of WSOC reported here were corrected for the field blanks. The relative differences for WSOC values in duplicate samples were < 5%.

2.6. Measurements of Major Inorganic Ions

For determination of inorganic ions, another filter cut (14 mm diameter) was extracted by Milli-Q water (10 ml) in plastic container with the ultrasonication. The total extract was filtrated through a membrane disc filter (Millex-GV, 0.45 µm, Millipore) and injected to ion chromatography (Model 761 compact IC; Metrohm, Herisau, Switzerland) for measuring major anions and cations [*Miyazaki et al*., 2009]. Anions were separated on a SI-90 4E Shodex column (Showa Denko, Tokyo, Japan) using a mixture of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ as an eluent at a flow rate of 1.2 mL min^{-1} and 40 mM H_2SO_4 as a suppressor. For cation measurements, a Metrosep C2-150 (Metrohm) column was used by using a mixture of 4 mM tartaric acid and 1 mM 2,6-pyridinedicarboxylic acid as an eluent at a flow

rate of 1.0 mL min^{-1}. The injection loop volume was 200 μL for both columns. The concentrations of the ions reported here are corrected for the field blanks.

2.7. Quality Assurance

To observe the analytical error and method accuracy, some experiment has been conducted like as a real sample analysis. Laboratory blank filers (n = 3) were analyzed to check the contamination during analysis. Significant contamination was not found in laboratory blank filter analysis. Values of 100 – 200 ng of each standard were spiked to 20 mm (dia) of blank filter and treated as a real sample. This recovery experiment was repeated three times. Recovery for major compounds is discussed in individual chapter. The field blank filters (n = 3) were also analyzed by the procedure described earlier in this chapter. Target compounds were not detected in the blank filters. Relative standard deviations for the target compounds in duplicate samples (n = 3) were generally < 10%.

2.8. Backward and Forward Trajectories and Fire counts

Seven-day air mass backward and forward trajectories were calculated three days for each sample (starting time, middle time and ending time) from June 2008 – June 2009 using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (http://ready.arl.noaa.gov/HYSPLIT.php) (Fig. 2, 4). The starting height of the trajectories is 500 m above the ground. Six hourly archived Global Data Assimilation System (1° x 1°) from the National Centers for Environmental Prediction (http://ready.arl.noaa.gov/gdas1.php) were used as meteorological data. Cluster analyses were further applied to better illustrate the characteristic air mass origins, in which three seed clusters (centroids) were generated in each season (Fig. 3).

In order to investigate the influence of biomass burning from different parts of North America and Siberia in ambient aerosols of Alaska, burning activities were illustrated by fire

spots, whose data were obtained from Fire Information for Resource Management System (FIRMS) operated by National Aeronautics and Space Administration (NASA) of the United States (https://earthdata.nasa.gov/data/near-real-time-data/firms) (Fig. 3).

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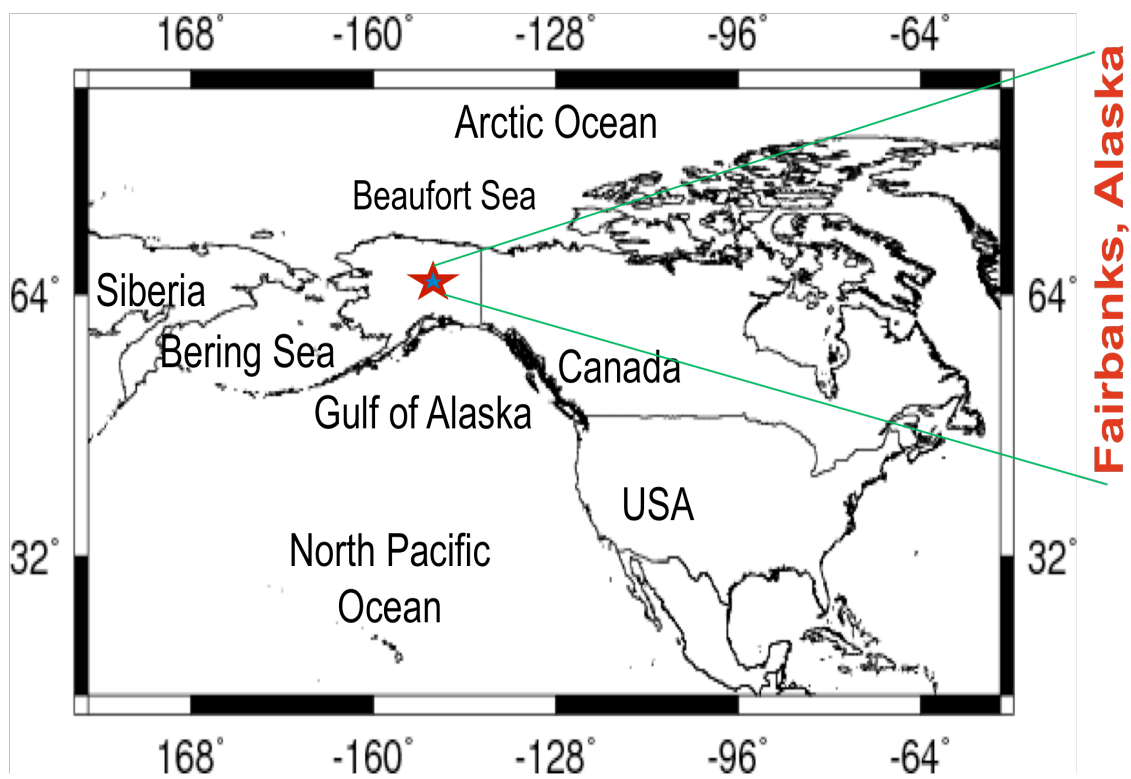
Fig. 1. Location of Fairbanks, Alaska , where aerosols particles were collected.
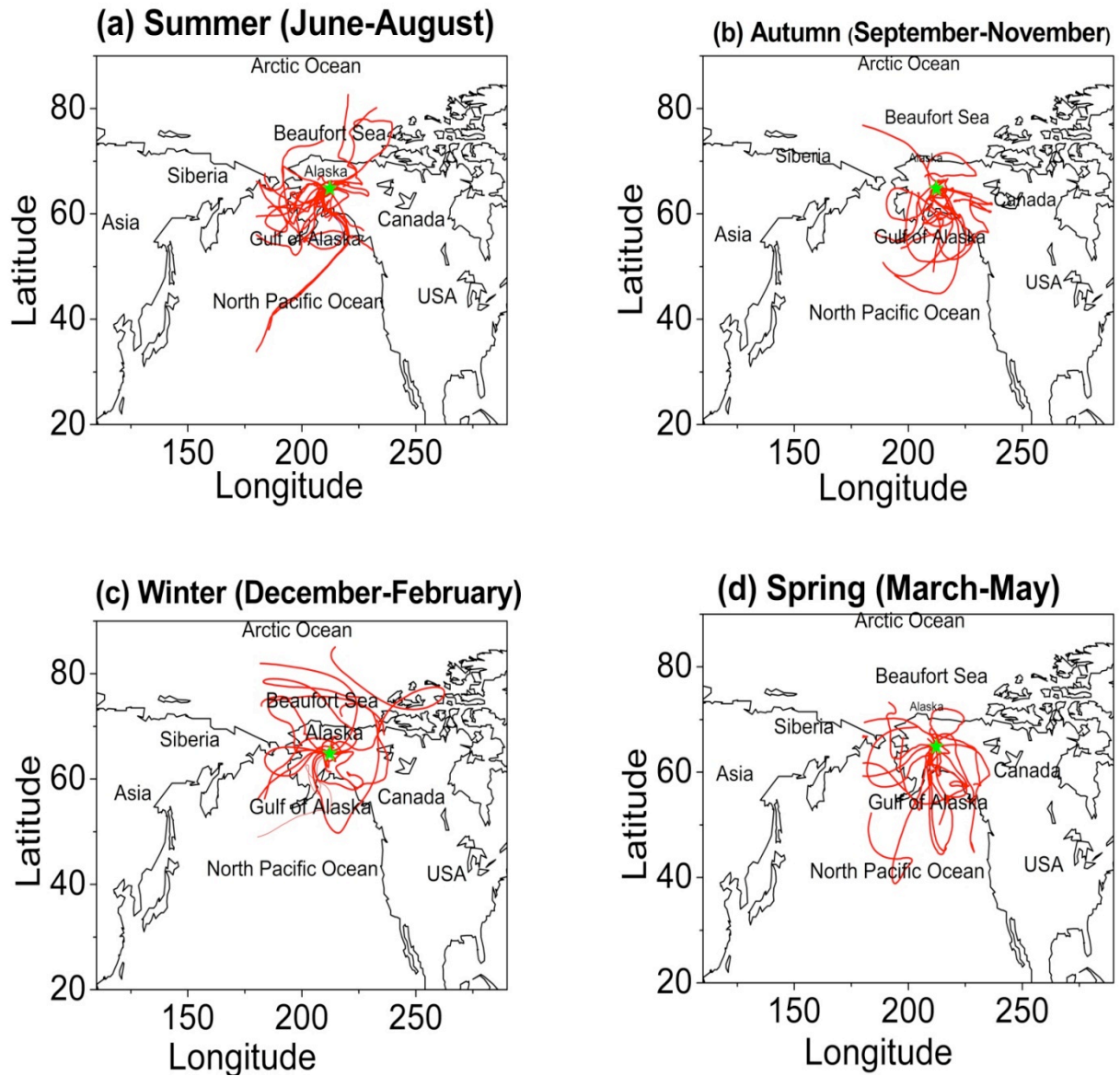
Fig. 2. 7 day backward air mass trajectories arriving at 500 m above the ground level
to Fairbanks, Alaska during June 2008 – June 2009.
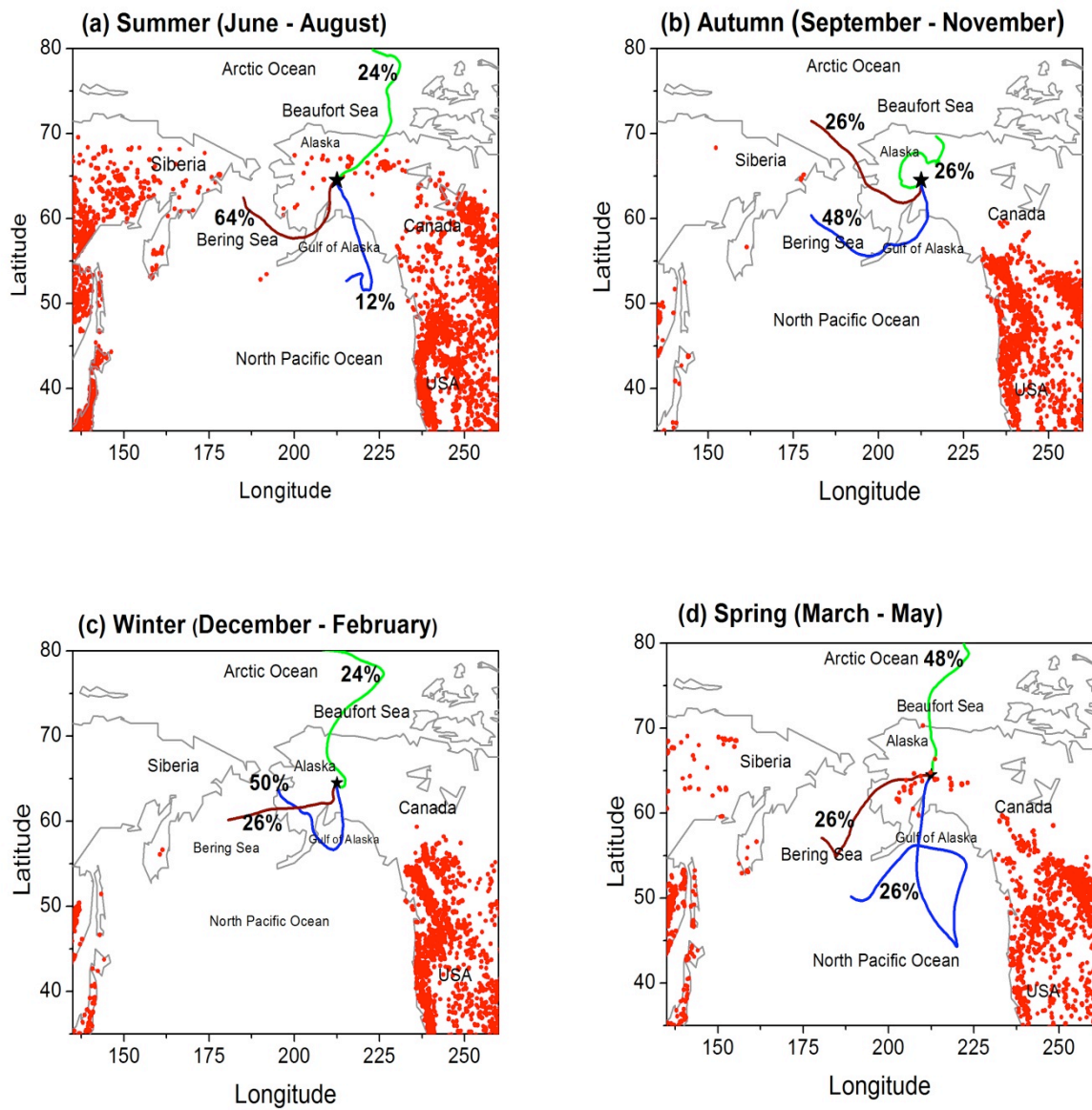
Fig. 3. 7 day backward air mass trajectories arriving at 500 m above the ground level to Fairbanks, Alaska shown by cluster during June 2008 – June 2009. The numbers in each panel indicate the percentages of trajectories in each season. Red color indicates the fire spots.
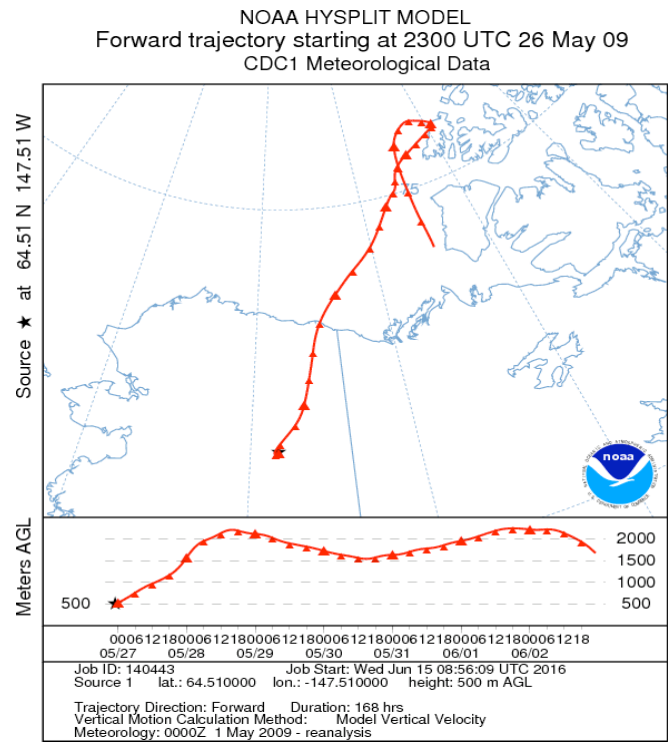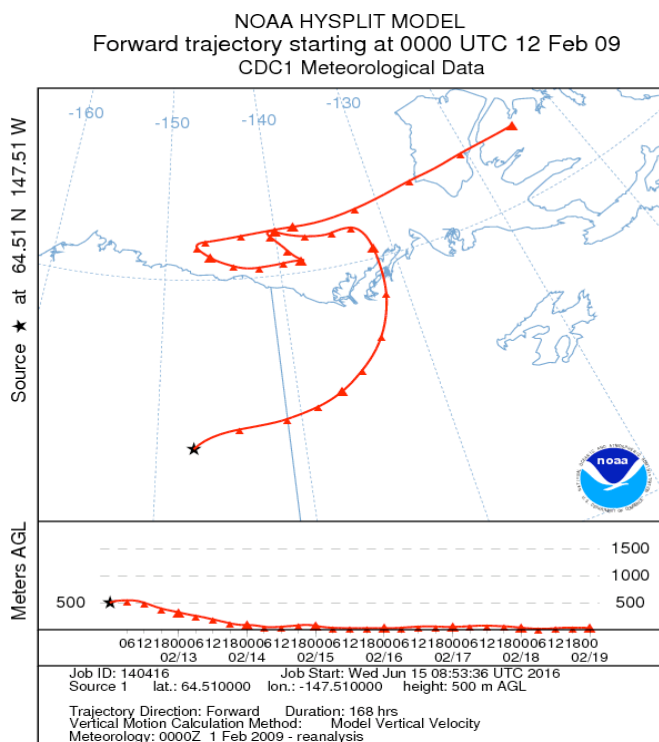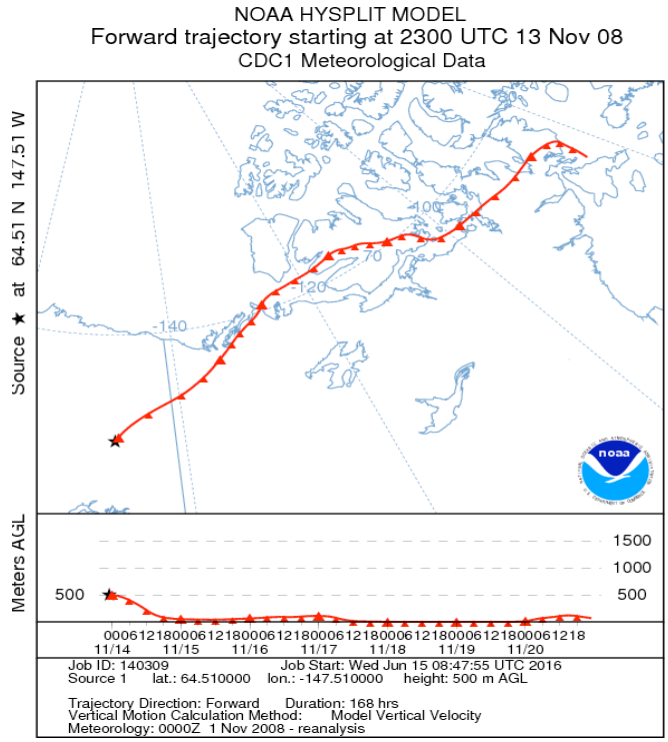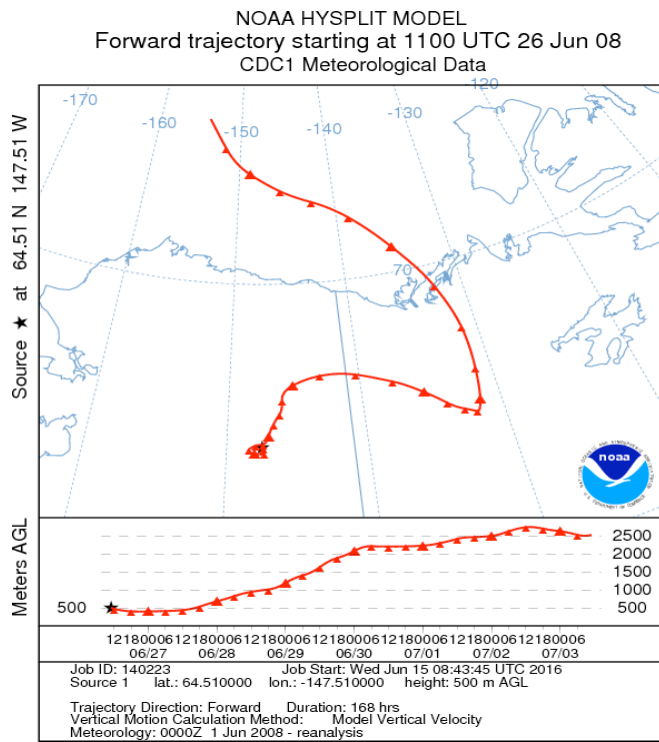
Fig. 4. 7 day forward air mass trajectories from Fairbanks, Alaska during June 2008 – June 2009 at 500 m above the ground level.

Chapter 3: Biomass burning is an important source for organic aerosol in sub-arctic Alaska

3.1. Introduction

Biomass burning (BB) is the burning of living and dead vegetation which releases large amounts of particulates and gases in the atmosphere. On the global budget, biomass burning contributed more than 90% of organic carbon (OC) released to the atmosphere [*Bond et al., 2004*]. Inventory studies suggested that biomass burning is the largest source of global black carbon (BC) emission [*Bond et al., 2004*], while recently highlighted biomass burning is also an important source of brown carbon [*Cheng et al., 2013*]. Biomass burning articulates impact climate and can also affect human health when they are inhaled, causing respiratory problems. There are several types of biomass burning, including open-field fires in forests, savannas, peat lands, burning of agricultural wastes in the fields burning, and residential heating and cooking, as well as industrial biofuel burning [*Akagi et al., 2011; Engling et al., 2014*].

Laboratory studies [*Grieshop et al., 2009*] observed that organic aerosol concentrations in diluted wood burning emissions increased by a factor of 1.5 to 2.8 after several hours of exposure to UV light and typical summertime hydroxyl radical (OH) concentrations, suggesting significant production of SOA from biomass burning emission. During aging processes, the formation of SOA from biomass burning emissions was also confirmed by field observations [*Adler et al., 2011; Lee et al., 2008*]. Recent studies also focusing on the precursors and formation pathways of SOA from biomass burning such as aqueous-phase reactions of phenolic compounds, which are emitted in large amounts from wood combustion, can form SOA at high yields [*Sun et al., 2010*]. Recently, a series of international research initiatives about biomass burning were conducted, such as the SAFARI (the Southern Africa Fire Atmosphere Research Initiative).

Several tracers have been used for BB such as anhydrosugars [*Engling et al.*, 2006; *Engling et al.*, 2009; *Fu et al.*, 2012; *Mochida et al.*, 2010], resin acids [*Kawamura et al.*, 2012; *Zhang et al.*, 2013] and water-soluble non-sea-salt potassium (nss-K^+) [*Sullivan et al.*, 2011; *Urban et al.*, 2012; *Zhang et al.*, 2013]. Levoglucosan (1,6-anhydro-*β*-D-glucopyranose), one of the anhydrosugars, is a thermal degradation product of cellulose and a unique tracer of particulate matter emissions from biomass burning. This compound is stable in the atmosphere over 10 days in acidic conditions [*Schkolnik and Rudich*, 2006]. However, recent studies, demonstrated that degradation of levoglucosan occurred from the exposure to high loading of hydroxyl radicals (OH) in the atmosphere and it can also be degraded during atmospheric transport [*Zhu et al.*, 2015]. Mannosan and galactosan are the isomers of levoglucosan can also be generated from pyrolysis of cellulose and hemicelluloses and used as BB tracers [*Engling et al.*, 2009; *Fabbri et al.*, 2009]. Phenolic compounds such as vanillic and hydroxybenzoic acids are derived during combustion of lignin which are detected in aerosols collected from urban and rural areas [*Nolte et al.*, 2001]. Dehydroabietic acid is also emitted to the atmosphere during the burning process of conifer resins [*Simoneit et al.*, 2002].

Wildfires have been a natural part of the boreal forest ecosystems, burning an average of 1 million ha/yr in 1950 increasing to almost 3 million ha/yr in 2000 in the North American boreal forests [*Kasischke and Stocks*, 2000]. Moreover, an increasing trend of fire occurrence and area burned has also been observed over Alaska boreal region from past years [*French et al.*, 2002]. The forest fires in boreal taiga enhance to the melting of permafrost under the forests and release on of the strong greenhouse gas methane stored under the frozen soil [*Kawamura et al.*, 2012]. Countries bordering the Arctic – i.e., the Scandinavian countries, Canada, USA and Russia – are well known to use large amounts of wood for residential heating [*Yttri et al.*, 2014]. Some previous studies also proposed that residential wood burning is more widespread and contributes more to the ambient aerosol's particulate matter

[*Sillanpää et al.*, 2006; *Gelencsér et al.*, 2007; *Puxbaum et al.*, 2007; *Lanz et al.*, 2010; *Maenhaut et al.*, 2012; *Genberg et al.*, 2013]. The International Atomic Energy Agency (2008) reported that the consumption of biomass is likely to increase by approximately 200% between 2000 and 2020, due to compensate for reductions in the use of fossil fuels.

The objective of this study is to characterize the abundance and seasonal variations of biomass burning tracers such as anhydro-sugars (Fig.1) and lignin & resin acids (Fig. 2) that are generated from combustion of wood or vegetation burning in the ambient aerosols from sub-arctic Alaska. Here, we interpret the possible source of biomass burning tracers based on fire spots and air mass back trajectories. We also discuss the contribution of biomass burning tracers to the Arctic and sub-arctic region based on air mass forward trajectories.

3.2. Experimental

3.2.1. Extraction and Derivatizations

The extraction process has been discussed in chapter 2.

3.2.2. Compound Identification

The target compounds were identified by using gas chromatography-mass spectrometry GC-MS) technique (see chapter 2). The mass fragmentation ions of m/z = 217, 204, 333 were used for the quantification of anhydro-sugars such as levoglucosan, galactosan, and mannosan, whereas m/z = 193, 223, 267, 282 for 4-hydroxybenzoic acid, m/z = 297, 312, 342 for vanillic acid, m/z = 327, 312, 342 for syringic acid and m/z = 239 for dehydroabietic acid. Recoveries of the target compounds were better than 80%. The data reported here were not corrected for recoveries. Levoglucosan was used as a surrogate standard for mannosan and galactosan.

3.3. Results and Discussion

3.3.1. Molecular compositions of biomass burning tracers

Two types of biomass burning tracers- a) anhydro-sugars and b) lignin and resin acids were identified in the Alaska aerosol samples (Table 1). Levoglucosan has been used as a general tracer of biomass burning in atmospheric aerosols [*Fu et al.*, 2008; *Simoneit*, 2002]. Galactosan and mannosan are also emitted to the atmosphere by the combustion of hemicellulose [*Kawamura et al.*, 2012; *Simoneit*, 2002]. The concentrations of anhydro-sugars such as levoglucosan, mannosan and galactosan were found to be 1.07-273 ng m^{-3} (ave. 66.8 ng m^{-3}), 0.22-63.1 ng m^{-3} (ave. 15.0 ng m^{-3}) and 0.12–39.4 ng m^{-3} (ave. 9.88 ng m^{-3}), respectively, which is higher than that reported in the Canadian High Arctic [*Fu et al.*, 2009]. Levoglucosan was found as the dominant biomass burning tracers followed by its two isomers: mannosan and galactosan. Time series concentrations for the anhydro-sugars are shown in Fig. 3. All anhydro-sugar compounds showed very similar temporal trends. The concentrations of these compounds seem to be increase in September with high peak in December and then decrease in March as well as again increase in June. Levoglucosan showed strong correlation with mannosan (r = 0.98, p < 0.001) and galactosan (r = 0.94, p < 0.001), indicating that they were derived from similar emission sources (Fig. 4). The concentration levels of levoglucosan in Alaska are higher than other sites of Arctic (Table 2).

Dehydroabietic acid is another tracer of biomass burning which can be used as a more specific tracer of the burning of conifer trees [*Kawamura et al.*, 2012]. This acid is produced during the combustion of conifer resin [*Simoneit et al.*, 2002]. The concentrations of dehydroabietic acid ranged from 0.00 to 50.5 ng m^{-3} with average of 8.51 ng m^{-3} (Table 1). Syringic, vannilic and 4-hydroxybenzoic acids are produced by incomplete combustions of lignin [*Simoneit et al.*, 2002]. The concentrations of syringic, vannilic and 4-hydroxybenzoic acids were found to be 0.00-20.5 ng m^{-3} (ave. 1.08 ng m^{-3}), 0.00-49.0 ng m^{-3} (ave. 3.36 ng m^{-3}

^{3}) and 0.35–17.7 ng m^{-3} (ave. 2.08 ng m^{-3}), respectively (Table 1). The lignin and resin products exhibited similar temporal trends with levoglucosan (Fig. 5). Significant correlations also observed between levoglucosan and lignin & resin products, suggesting that their maximum portion come from the similar sources (Fig. 6).

3.3.2. Seasonal variations of biomass burning tracers

Clear seasonal variations were found in the concentrations of anhydro-sugars detected in the aerosol samples from Alaska (Fig. 7). The seasonally averaged concentrations of levoglucosan were significantly higher in winter (ave. 145 ng m^{-3}) and autumn (129 ng m-3) than summer (32.6 ng m^{-3}) and spring (12.3 ng m^{-3}). The seasonal variations of mannosan and galactosan were similar to those of levoglucosan, whereas their concentrations are four to five times lower than levoglucosan (Table 1). Lignin and resin acids such as dehydroabietic, vanillic, syringic and 4-hydroxybenzoic acids also showed similar seasonal variations with levoglucosan in winter maximum followed by autumn, summer and spring (Fig. 8). During winter and autumn, very less fire spots were observed in Alaska region. Satellite observation can detect only open burning. *Yan et al.* [2006] reported that satellite observation detected only < 1% of the burning of total crop residues recorded by ground observation survey, due to a large portion of indoor burning that could not be detected by satellite. Indoor burning for residential heating in Alaska may have largely contributed to biomass burning tracers during cold season. Backward trajectory clusters indicate that 50% and 26% of the air masses were originated shorter distances around Alaska region in winter and autumn, respectively, whereas the remaining air masses were transported longer distances from Oceanic regions. These results demonstrated that high levels of biomass burning tracers in winter and autumn time are associated with domestic burning for residential heating.

In contrast, backward trajectory in summer and spring indicates that air mass mainly come from the Oceanic region when fire spots were observed around Alaska region (Chapter

2, Fig. 2, 3). The fire spots indicate open burning mainly forest fire. Thus, during summer and spring time biomass burning tracers might be emitted from forest fire. Wet deposition is one parameter that can controls the atmospheric levels of BB tracers [*Hu*, 2013]. However, wet deposition alone could not result in such a large seasonal difference of biomass burning tracers. Degradation by OH radical can explain the lower level of biomass burning tracers during summer and spring period. A higher level of OH in the troposphere is expected in summer as a result of higher ambient temperature, stronger ultraviolet light and relative humidity conditions [*Stone et al.*, 2012], which would enhance to the degradation of levoglucosan [*Hennigan et al.*, 2010; *Hoffmann et al.*, 2010; *Mochida et al.*, 2010]. Based on laboratory experiments, *Hoffmann et al.* [2010] proposed that the degradation rate of levoglucosan by OH radicals to be 7.2 ng m^{-3} h^{-1} in summer and 4.7 ng m^{-3} h^{-1} in winter.

I calculated levoglucosan/mannosan (L/M) ratios to distinguish the possible source difference of biomass burning tracers in the Alaska aerosol samples. The L/M ratios ranged from 2.30 to 7.84, were not exhibited any seasonal variations in this study (Fig. 12). During cold season paper birch (deciduous tree) and white spruce (conifer tree) are used for domestic burning in Alaska region. The plant species are soft wood and have a wide range in Alaska and Canada. Several studies reported that L/M ratios could be used for discriminating hard wood and soft wood burning [*Kuo et al.*, 2011]. As hard wood contains higher amount of cellulose (55-65%) compare to hemicellulose (20-30%) [*http://bioenergy.ornl.gov/main.aspx*; *Klemne et al.*, 2005; *Sjostrom*, 1993], high level of levoglucosan is derived by thermal decomposition of hard wood. Thus, higher L/M ratios indicate hard wood burning and lower ratios for soft wood burning. In a chamber experiment, *Schmidl et al.* [2008] observed L/M ratios of 3-5 for soft wood and 14-15 for hard wood burning. The L/M ratios of 3-5 for soft wood, > 10 for hard wood and up to 50 for some herbaceous plants were reported by *Engling et al.* [2009]. *Sheesley et al.* [2003] and *Zhang et al.* [2007] proposed L/M ratios of 41.6 and

55.7 for rice straw and cereal straw burning, respectively. Based on the above discussions, it can be hypothesized that the biomass burning tracers in Alaska aerosols mainly derived from soft wood burning.

3.3.3. Relations between levoglucosan and inorganic ions, carbonaceous components

Linear correlations among levoglucosan and major ions that are possibly related to biomass burning were observed. Nss-K^+ is another typical tracer of biomass burning [*Sullivan et al.,* 2011]. However, poor correlation between levoglucosan and nss-K^+ (r = 0.32, p = 0.07) were found in this study due to the presence of other K^+ sources such as soil dust, vegetation etc. or different types of burning materials. Previous studies also reported that soil dust could be another source of water-soluble nss-K^+ [*Arimoto et al.,* 2004; *Duvall and Simoneit,* 2008; *Shen and Liu,* 2009]. The emission of K^+ from biomass burning also depends on burning materials and burning process [*Zhang et al.,* 2010]. Smoldering combustion produce more unbroken organic compounds compared to flaming process, thus yield more levoglucosan in comparison to nss-K^+ [*Cheng et al.,* 2013]. The correlations between levoglucosan and nss-K^+ were further investigated for seasonal profiles (Fig. 9).

Biomass burning is an important source of reactive nitrogen which can produce NH_3, NO_x etc., in the atmosphere [*Goode et al.,* 2000]. Positive relations were observed between levoglucosan and NH_4^+ (r = 0.65, p < 0.001), indicating that biomass burning could be an important direct source of NH_4^+ [*Andreae and Merlet et al.,* 2001; *Akagi et al.,* 2011] (Fig. 10). NH_4^+ could also be formed by the protonation of NH_3 in the atmosphere, which is abundantly emitted from biomass burning, livestock excreta, agricultural soil and plants, fertilizer application, etc. [*Asman et al.,* 1998; *Huang et al.,* 2012; *Paulot et al.,* 2014; *Sutton et al.,* 2008]. Levoglucosan also showed significant correlation with NO_3^- (r = 0.82, p < 0.001), suggesting high emission of NO_x during biomass burning activities in Alaska (Fig. 10). NOx can also be derived from automobiles [*Reddy et al.,* 2012].

Organic carbon (OC), water-soluble organic carbon (WSOC) and elemental carbon (EC) exhibited similar temporal trends with high abundant in winter and summer (Chapter 4, Fig. 2). Levoglucosan showed significant correlation with OC ($r = 0.51$, $p < 0.001$), WSOC ($r = 0.61$, $p < 0.001$) and EC ($r = 0.67$, $p < 0.001$), indicating that biomass burning is an important source for carbonaceous compounds (Fig. 11). WSOC is a major part in atmospheric aerosols that contributes to the number density of cloud condensation nuclei. Positive relations of WSOC with levoglucosan suggest that WSOC in Alaska aerosols is substantially derived from biomass burning. Previous study also reported that main contributors to WSOC are probably biomass-burning tracers and secondary organic aerosol, due to their preferentially association with the fine fraction [*Mkoma et al.*, 2013]. Biomass burning is frequently accompanied by abundantly emissions of EC [*Akagi et al.*, 2011]. The transportation of black carbon (BC) aerosols (soot) from central Alaska to the Arctic Oceanic region indicates that higher emission of BC from Alaska biomass burning activities [*Kim et al.*, 2005]. Another source of EC is from coal combustion and motor vehicle exhaust [*Zhu et al.*, 2015]. Significant correlation between levoglucosan and EC demonstrate that biomass burning in Alaska might be a more important source for EC. The ratios between levoglucosan and OC, EC (L/OC, L/EC) are showing similar temporal trend with levoglucosan in winter maximum (Fig. 12). This result also suggests that the emission of OC and EC in the Alaska atmosphere is more influenced by biomass burning.

3.3.4. Contributions of biomass burning to WSOC and OC

The levoglucosan to OC (L/OC) ratio has been evaluated to the contribution of different BB sources [*Sullivan et al.*, 2008; *Mkoma et al.*, 2013; *Ho et al.*, 2014] and possible aging of levoglucosan [*Mochida et al.*, 2010]. Using levoglucosan as a representative of biomass burning tracers, the contributions of biomass burning tracers to WSOC and OC were examined with seasonal basis. A clear seasonal trend of L/OC suggests that the contribution

of biomass burning tracers to OC varied depending on season (Fig. 12). We further calculated the contributions of levoglucosan carbon to OC and WSOC in the Alaska aerosols. In this study, the levoglucosan annually account for 0.06-9.23% (ave. 2.92%) of the WSOC and 0.03-4.87% (1.62%) of the OC, which is higher than those of the Pearl River Delta sites in China (levoglucosan-C/WSOC of 0.59-3.12%) that are directly influenced by biomass burning in southern china [*Ho et al.*, 2014]. The contributions of levoglucosan to OC were found to be highest in winter (3.63%) followed by autumn (3.18%), summer (0.60%) and spring (0.51%). The contributions of levoglucosan to WSOC also exhibited similar seasonal variability when highest value observed in winter (6.26%) followed by autumn (5.62%), summer (1.31%) and spring (0.84%).

The lower contributions of biomass burning tracers to OC in spring and summer demonstrated that biogenic secondary organic aerosol (SOA) tracers and primary sugars/sugar alcohols probably contribute more in these seasons due to the blooming time of vegetation. These results are consistent with the higher concentrations of SOA tracers and sugar compounds in summer and spring (chapter 4, 5). The values of contributions biomass burning to OC are comparable to other studies that are reported for biomass burning activities from various sites [*Andreae and Merlet*, 2001; *Zhang et al.*, 2008, 2012; *Reche et al.,* 2012]. A further estimation on the OC components by positive matrix factorization (PMF) analysis can provide more useful information, which is described in chapter 6. On the based on these results, it can be proposed that biomass burning is a significant contributor to OC in the Alaska aerosols, especially in winter, might be affected regional air quality.

3.4. Summary

In this study, three anhydro-sugars such as levoglucosan, galactosan and mannosan as well as four lignin and resin products such as dehydroabietic, vanillic, syringic and 4-hydroxybenzoic acids are reported as biomass burning tracers in the Alaska aerosol samples. Levoglucosan was found to be one of the most abundant species among the other biomass burning tracers with a concentration range of 1.07-273 ng m^{-3} (average 66.8 ng m^{-3}) followed by its two isomers: mannosan (0.22-63.1 ng m^{-3}; ave. 15.0 ng m^{-3}) and galactosan (0.12–39.4 ng m^{-3}; ave. 9.88 ng m^{-3}). All anhydro-sugars exhibited similar temporal and seasonal trends with high abundant in winter and autumn. The result of levoglucosan showed clear seasonal variability with winter maximum (ave.145 ng m^{-3}) and spring minimum (12.3 ng m^{-3}). Similar temporal and seasonal variations with levoglucosan were observed for all lignin and resin acids. Dehydroabietic acid was detected as a most abundant tracer among all lignin and resin products. The amount of dehydroabietic acid were found to be 0.00 to 50.5 ng m^{-3} (ave. 8.51 ng m^{-3}) in annually, where as seasonally observed high level in winter (20.7 ng m^{-3}) and low level in spring (0.62 ng m^{-3}). Lignin & resin acids showed significant correlations with levoglucosan, suggesting that their source might be similar. The L/M ratios ranged from 2.30 to 7.84 indicate that the biomass burning tracers in the Alaska atmosphere mainly originated from soft wood burning.

The analyses of air mass back trajectories and fire spots demonstrated that biomass burning tracers may be associated from residential heating and cooking in regional area, especially in cold season. Significant correlations of levoglucosan with OC, EC and WSOC, suggesting importance of biomass burning for carbonaceous aerosols in Alaska atmosphere. Poor correlation between levoglucosan and nss-K$^+$ demonstrated that particular burning materials or burning process are occurred in Alaska region which can not emit K$^+$ in the atmosphere. Levoglucosan contributed 2.92% to WSOC and 1.62% to OC. The highest

values of WSOC (6.26%) and OC (3.63%) in winter time indicate that contribution of biomass burning to Alaskan aerosols is more important in winter period. These results provide useful information to better understand the effect of biomass burning on subarctic atmosphere.

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Table 1

Average concentrations of anhydro-sugars and lignin & resin acids (ng m^{-3}) measured in the Alaska Aerosols.

Species	summer			autumn			winter			spring		
	avg[a]	min	max	avg	min	max	avg	min	max	avg	min	max
anhydro-sugars												
levoglucosan	32.6	1.07	146	129	24.8	273	145	95.1	214	12.3	1.41	36.1
mannosan	6.79	0.42	31.3	28.1	4.04	63.1	36.2	17.1	54.0	2.08	0.22	6.29
galactosan	4.57	0.12	24.7	18.2	1.99	39.4	24.0	10.6	35.6	1.34	0.13	3.98
lignin & resin acids												
dehydroabietic acid	1.34	0.26	7.53	16.1	1.24	42.6	20.7	2.72	40.5	0.62	0.00	1.25
syringic acid	0.05	0.00	0.26	1.13	0.03	2.98	2.38	0.16	6.55	0.04	0.00	0.12
vannilic acid	0.44	0.05	2.50	4.05	0.17	9.66	7.66	1.31	15.7	0.26	0.00	0.50
4-hydrxybenzoic acid	1.24	0.38	2.72	2.08	0.61	3.44	3.28	1.91	5.65	1.09	0.35	2.24

[a]avg :average.
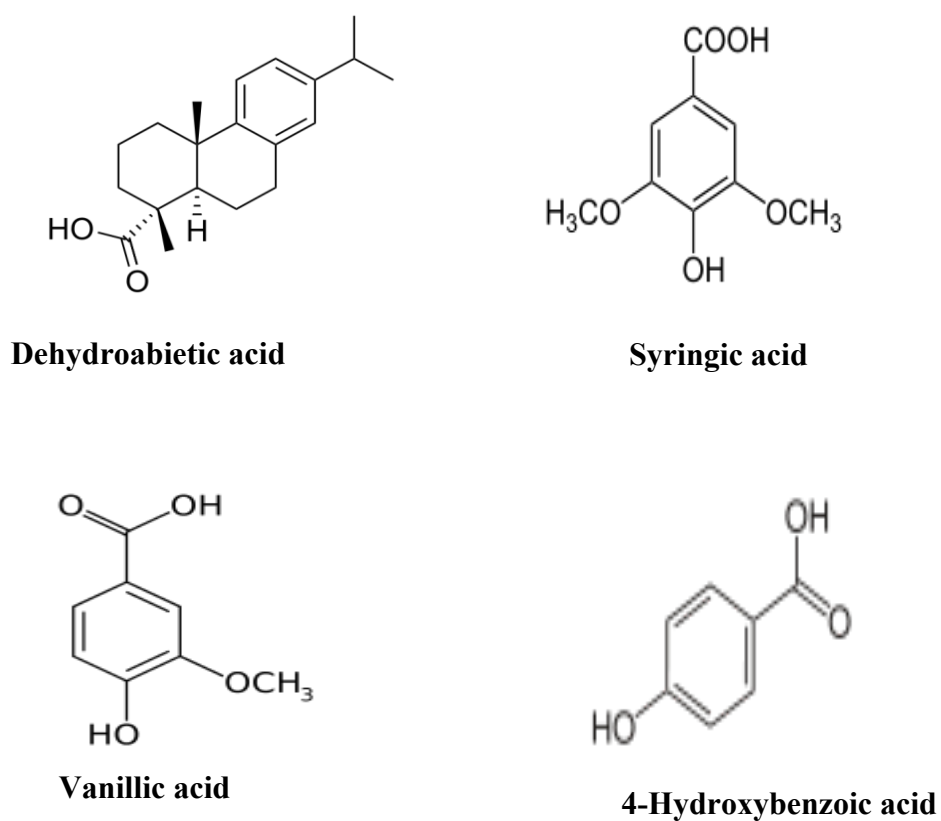
Table 2. Comparisons of the concentrations (ng m^{-3}) of levoglucosan in Alaska aerosols with those from different sites in Arctic and other regions.

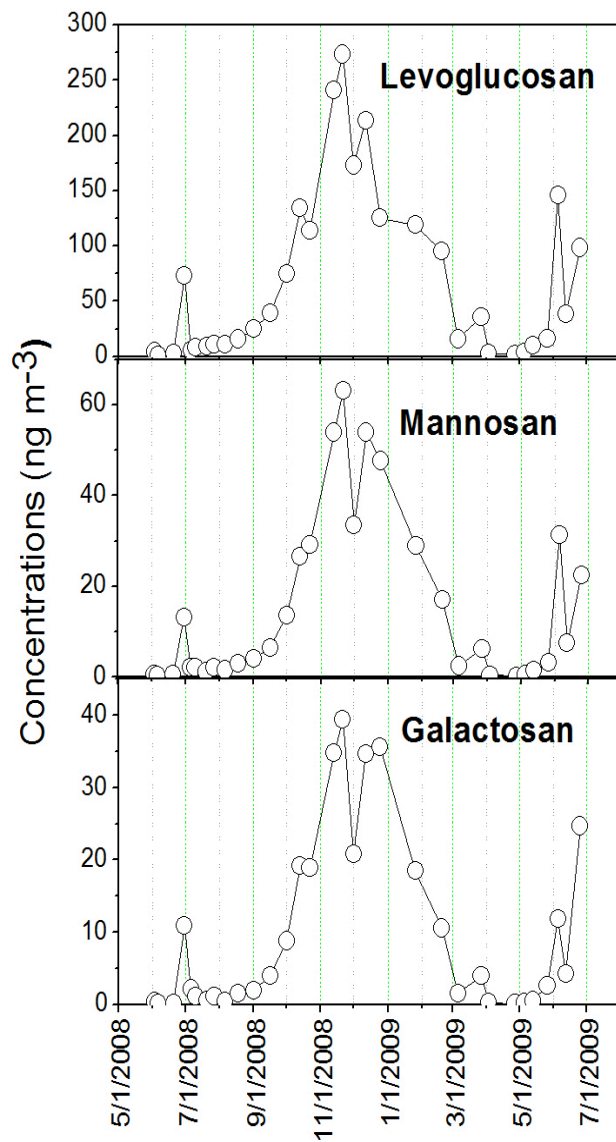| Location	Levoglucosan	References
Alaska, USA	1.07-273	This study
Alert, Canada	0.003-1.08	[*Fu et al.*, 2009]
Svalbard, Norway	0.07-3.20	[*Yttri et al.*, 2014]
Beaufort sea, Canadian Arctic	0.01-0.93	[*Fu et al.*, 2013]
Northern Hemisphere	1.1-41	[*Hu et al.*, 2013]
Texas, USA	200-1200	[*Matthew et al.*, 2000]
Southeast Asia	1.2-4.3	[*Hu et al.*, 2013]

Levoglucosan **Mannosan** **Galactosan**
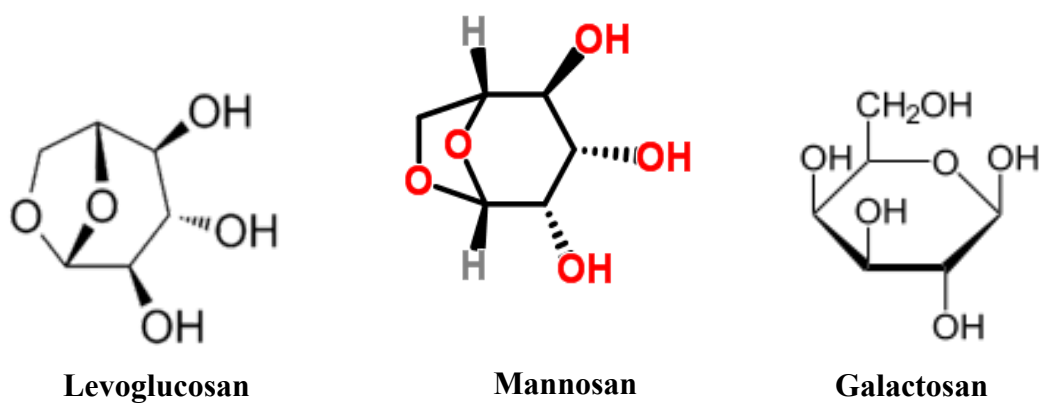
Fig. 1. Chemical structures of anhydro-sugars

Dehydroabietic acid **Syringic acid**
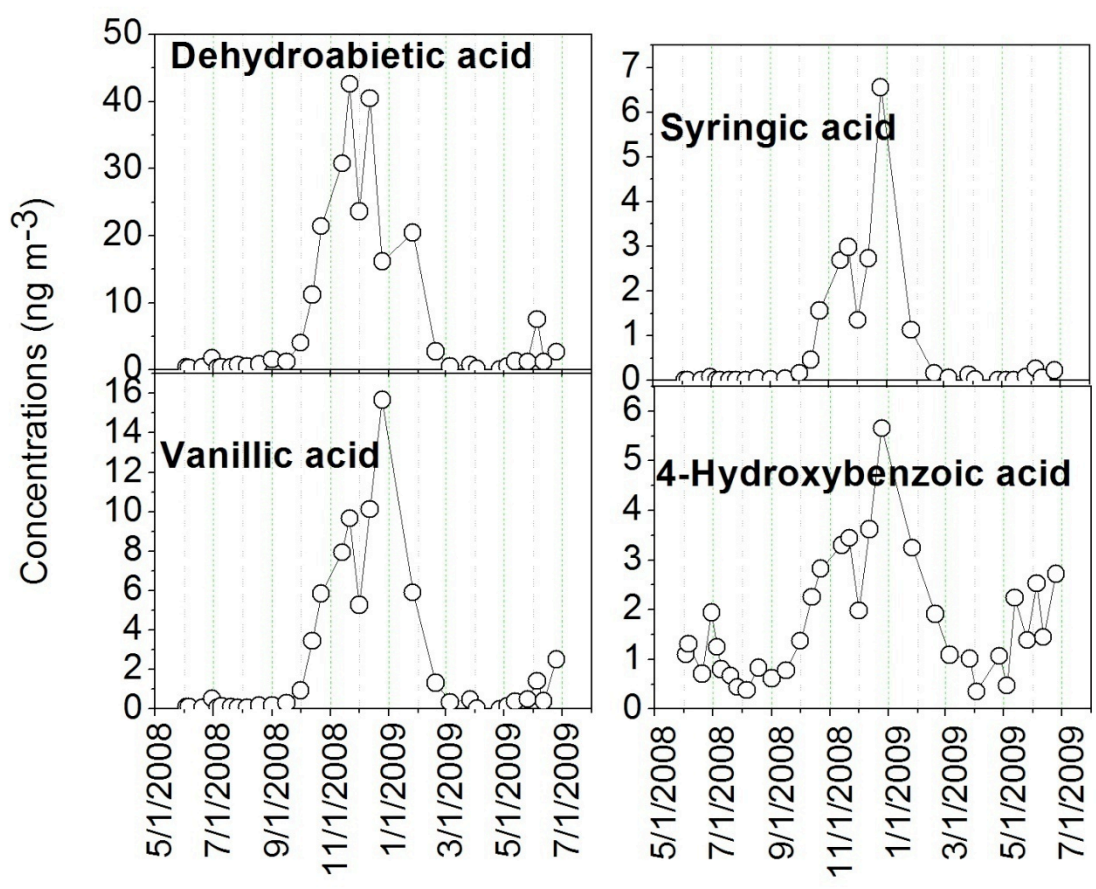

Vanillic acid

4-Hydroxybenzoic acid

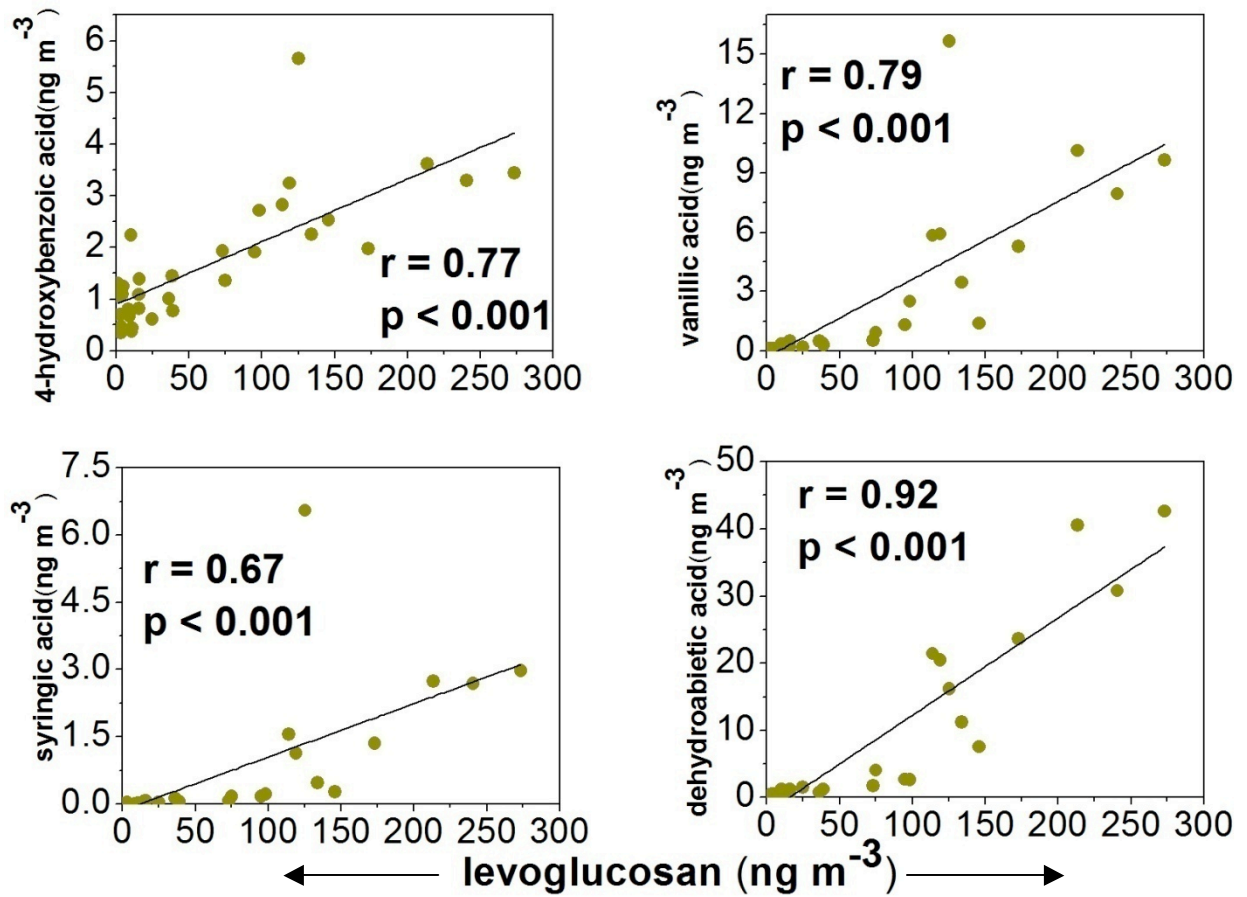**Fig. 2.** Chemical structures of lignin and resin acids

Fig. 3. Temporal variations of levoglucosan, mannosan and galactosan.
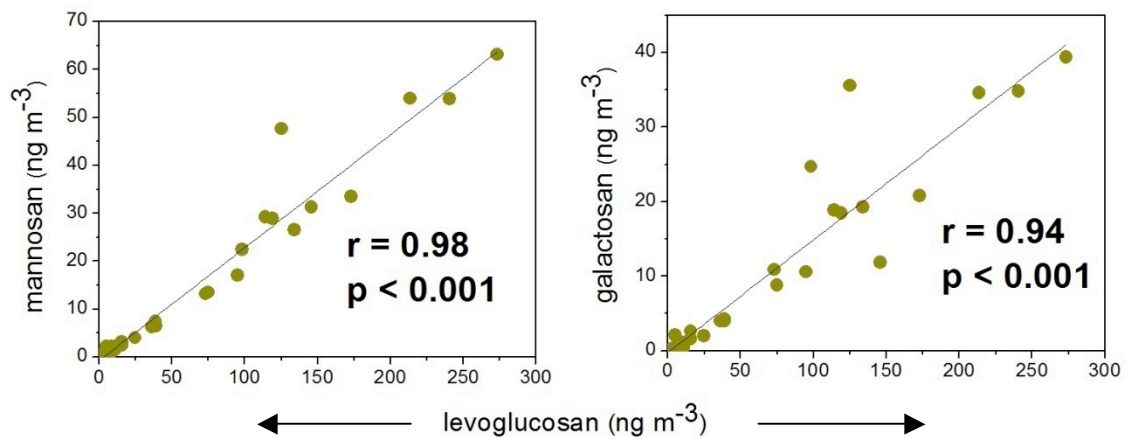
Fig. 4. Correlation among levoglucosan, mannosan and galactosan

Fig. 5. Temporal variations of dehydroabietic, vanillic, syringic and 4-hydroxybenzoic acids.

Fig. 6. Correlation between levoglucosan and lignin & resin products
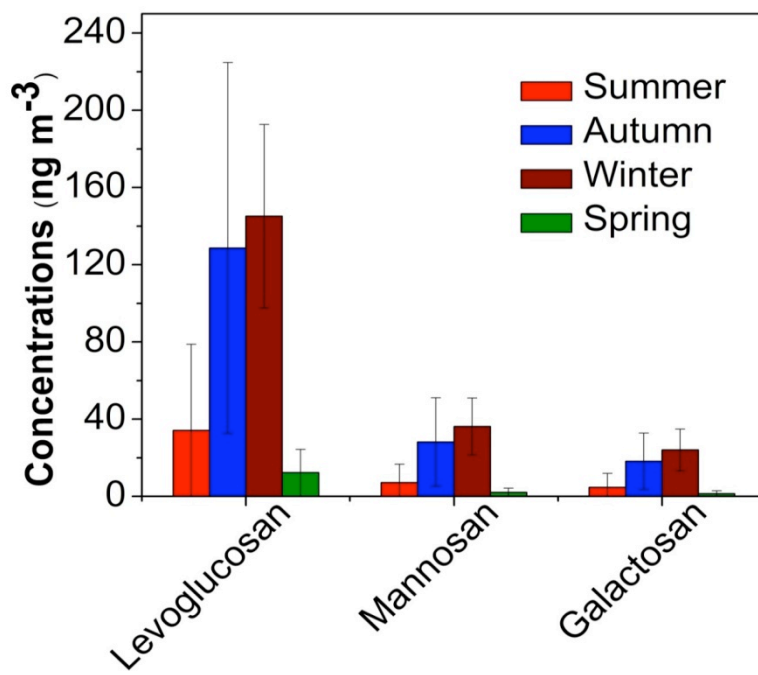
Fig. 7. Seasonal variations of anhydro-sugars

Fig. 8. Seasonal variations of lignin and resin acids
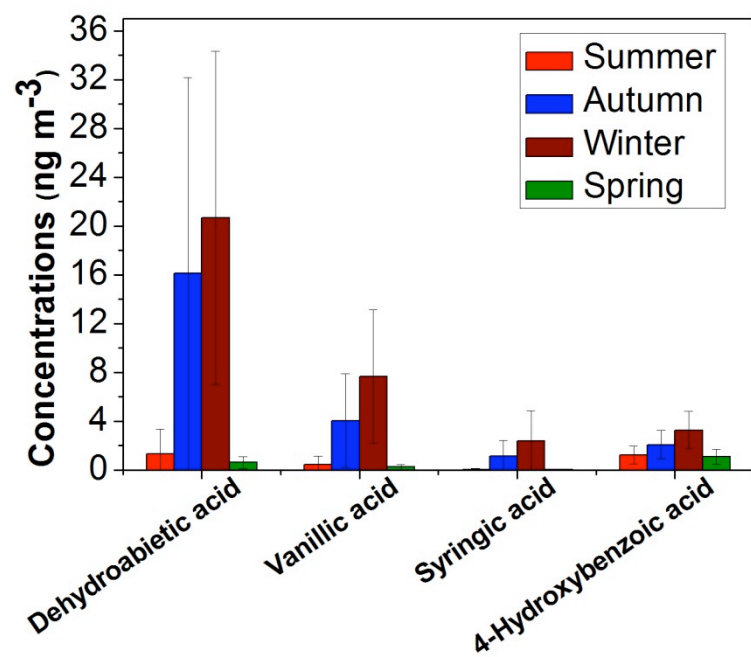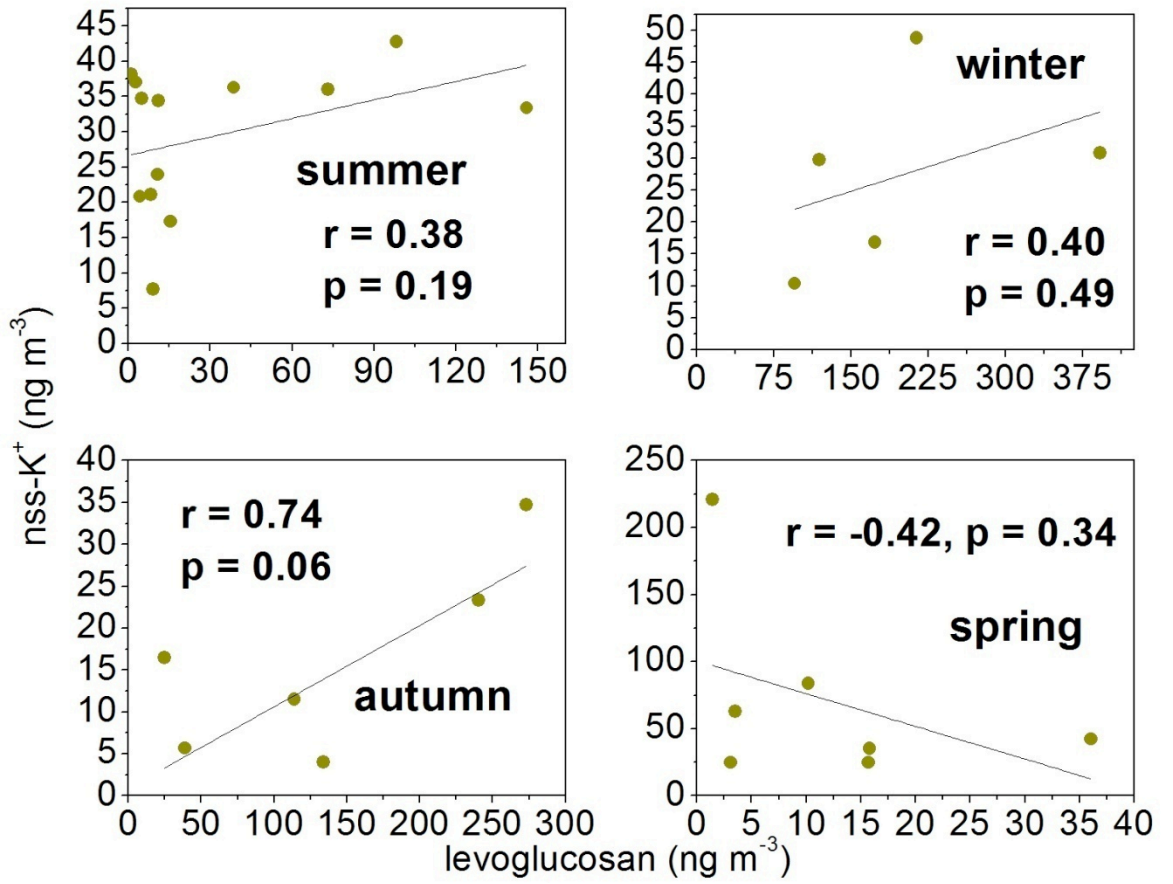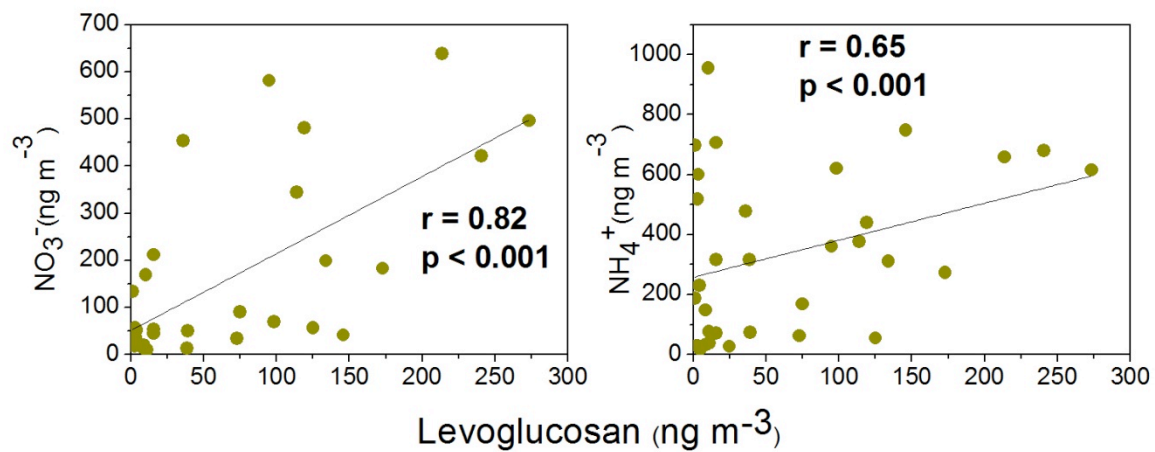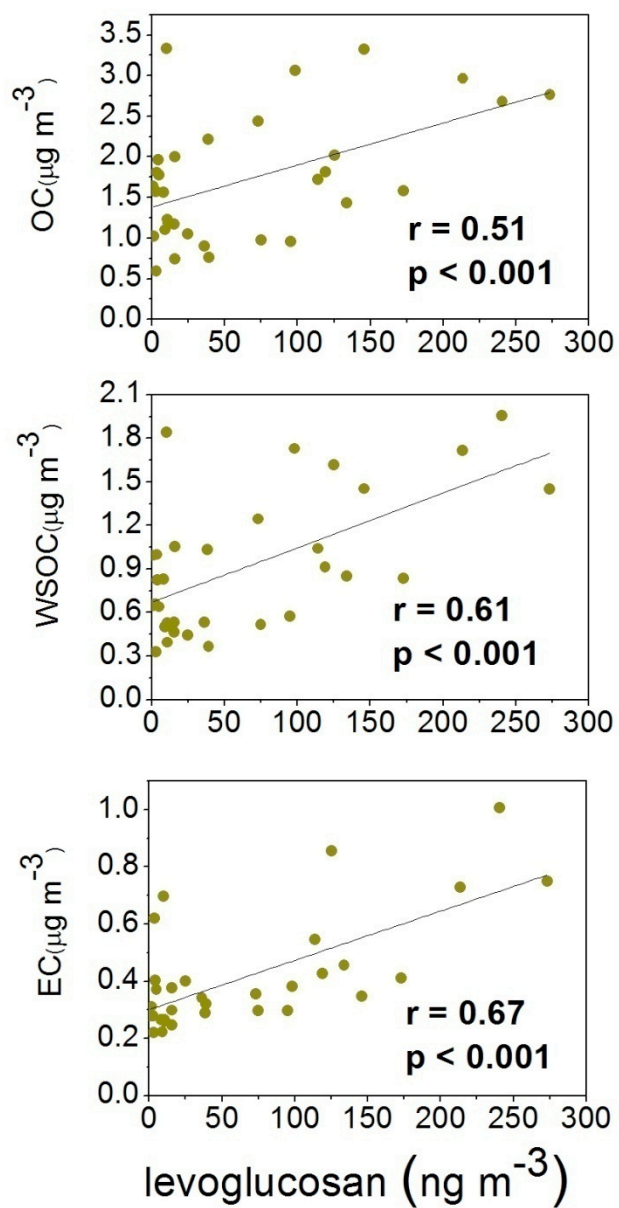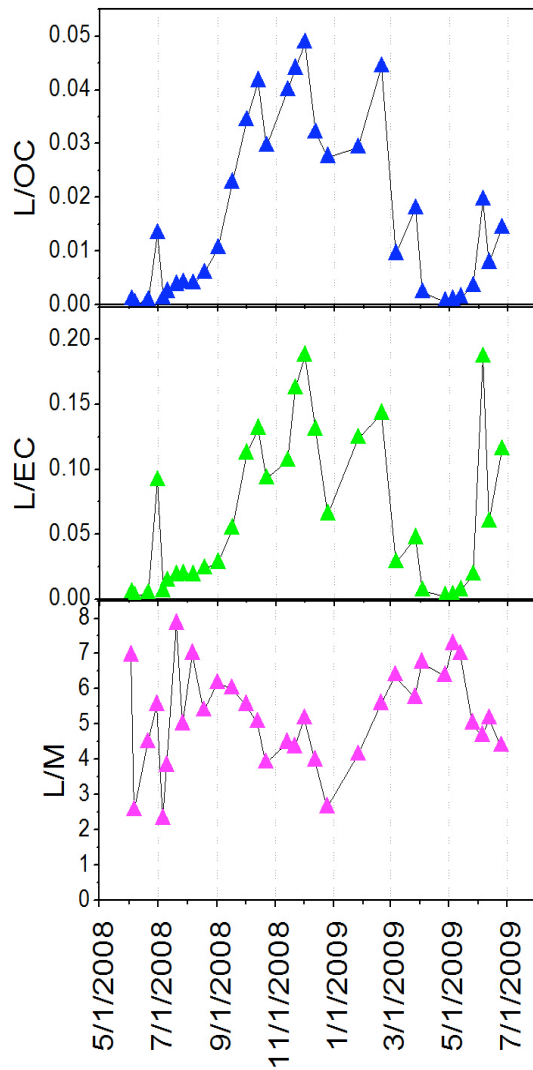
Fig. 9. Correlation between levoglucosan and nss-K$^+$

Fig. 10. Correlation between levoglucosan and NO_3^-, NH_4^+

Fig. 11. Correlation between levoglucosan and OC, WSOC, EC.

Fig. 12. Temporal trends of levoglucosan/OC (L/OC), levoglucosan/EC (L/EC) and levoglucosan/mannosan (L/M) ratios.

Chapter 4: Contributions of biogenic secondary organic aerosol (SOA) tracers in the Alaska atmosphere

4.1. Introduction

The organic compounds of secondary organic aerosol (SOA) may be derived from either biogenic or anthropogenic precursors, thus it is important to evaluate the contribution of both sources to understand SOA formation. Secondary organic aerosol (SOA) is a large fraction of organic aerosol are produced by homogenous [*Claeys et al.*, 2004] and heterogeneous [*Jang et al.*, 2002] reactions of volatile organic compounds (VOCs). On a global budget, emissions of biogenic VOCs (1150 Tg/yr) are suggested to be dominant over those of anthropogenic VOCs [*Guenther et al.*, 2006]. Vegetation can release huge amounts of BVOCs, including isoprene, monoterpenes, sesquiterpenes and oxygenated hydrocarbons [*Goldstein and Galbally*, 2007; *Guenther et al.*, 1995]. Oxygenated VOCs contribute to particle growth processes over boreal forests [*Kourtchev et al.*, 2008]. Photo-oxidation products of isoprene play an important role in the particle nucleation process [*went*, 1960], whereas monoterpene oxidation products are not nucleating organic species [*Marti et al.*, 1997; *Kulmala et al.*, 2001]. These BVOCs play an important role in local, regional, and global climate change by affecting the earth's radiative balance [*Hoyle et al.*, 2009] and leads to visibility reduction [*Kleindienst et al.*, 2007]. Global SOA are considered to be largely from BVOCs [*Farina et al.*, 2010]. However, anthropogenic contributions to SOA often exceed 50% in the urban areas due to the influence of human activities [*de Gouw et al.*, 2008; *Ding et al.*, 2012; *Volkamer et al.*, 2006]. Anthropogenic emissions in urban regions might be accelerated oxidation of BVOCs and SOA formation [*Carlton et al.*, 2010; *Hoyle et al.*, 2011; *Weber et al.*, 2007].

Isoprene is a significant source of organic aerosol in the atmosphere, with emissions estimated to be 440-660 TgC yr^{-1} [*Surratt et al.*, 2010]. On a global scale, the annual

emissions of biogenic VOCs (1150 Tg yr^{-1}) are suggested to be one order of magnitude higher than those of anthropogenic VOCs [*Guenther et al.*, 2006], consisting of 44% isoprene, whereas anthropogenic emissions were only 110 TgC/yr and contributions of aromatics were 13% among them [*Ding et al.*, 2014]. The oxidation of isoprene leads to the formation of SOA in the atmosphere via heterogeneous reactions [*Kroll et al.*, 2006] even though various factors such as different oxidants (OH, O$_3$ and NO$_3$), NOx concentration, etc. can play a role in SOA formation [*Kroll et al.*, 2006]. Contribution of photo-oxidation products of isoprene is significant to boreal forest aerosols [*Kourtchev et al.*, 2005]. 2-Methyltetrols were first identified in the Amazonian rainforest [*Claeys et al.*, 2004] and subsequently detected in ambient aerosols from many sites in the world [*Clements and Seinfeld,* 2007].

Monoterpenes and sesquiterpenes are also believed to be important sources of biogenic SOA. Monoterpenes are mainly emitted from conifer forest, with annual emission of 127 Tg, considering α-pinene as major terpene [*Claeys et al.*, 2007]. Several studies of organic aerosol composition have focused on monoterpene photo-oxidation products at coniferous forest sites [*Kavouras et al.*, 1998; *Yu et al.*, 1999; *Pio et al.*, 2001] and the emissions of monoterpene are believed to be important in these environments [*Jobson et al.*, 1994; *Lamanna and Goldstein*, 1999; *Hakola et al.*, 2000]. Monoterpene-SOA tracers have been used to evaluate the role of monoterpene in the formation of SOA; monoterpenes contribute about 35% of the global emissions of BVOCs [*Griffin et al.*, 1999]. It has been well established that photochemical oxidation and ozonolysis of monoterpenes can lead to secondary organic aerosol (SOA) formation [*Hoffman et al.*, 1997; *Kavouras and Stephanou*, 2002]. High SOA yields from monoterpene were also observed in laboratory experiments [*Griffin et al.*, 1999]. Moreover, the compositions of SOA tracers can give additional information on the process and sources [*Ding et al.*, 2014]. The ratio of 3-hydroxyglutaric

acid to 3-methyl-1,2,3-butanetricarboxylic acid can distinguish α-pinene from other monoterpenes [*Jaoui et al.*, 2005; *Lewandowski et al.*, 2013].

The boreal forest covers more than 1.2×10^7 km^2 spanning North America and Eurasia [*Baumgartner*, 1979; *Stocks and Lynham*, 1996], whereas two-thirds of area are located in Eurasia and the remaining is located primarily in Canada and Alaska [*Hare and Ritchie*, 1972]. Tundra and taiga forests are also available in Russia, Alaska and Canada. Thus, BVOC emissions from these ecosystems are considered to make a significant contribution to SOA mass. High loading of natural aerosols over boreal forests was proposed in northern Europe [*Tunved et al.*, 2006]. The contribution of BVOCs, especially terpenes to aerosol formation is important in northern remote areas [*Carlton et al.*, 2009; *Zhao et al.*, 2015]. Recent study suggested that BVOCs emission from subarctic ecosystems are more responsible for rising temperatures than elsewhere [*Faubert et al.*, 2010; *Penuelas and Staudt*, 2010; *Tiiva et al.*, 2008]. Although many studies have been conducted for the understanding the compositions, sources and formation mechanisms of SOA for the last decade, it is still needed to expand the knowledge on the SOA formation in the high latitudinal atmosphere.

The purpose of this study is to understand seasonal trend of SOA tracers that are derived from photo-oxidation of isoprene, *α*-/*β*-pinene, and *β*-caryophyllene in the ambient aerosols from Fairbanks, Alaska (Fig 1). Contributions of SOA tracers to organic carbon (OC), water-soluble organic carbon (WSOC) and secondary organic carbon (SOC) are also reported in the ambient aerosols over central Alaska.

4.2. Experimental

4.2.1. Extraction and Derivatization

Discussed in chapter 2.

4.2.2. Compound Identification

The compounds were identified by using GC-MS technique (Interpreted in chapter 2). For the quantification of *cis*-pinonic, pinic and 3-hydroxyglutaric acids, their GC-MS response factors were determined using authentic standards. Owing to a lack of standards, concentrations of 2-methylglyceric acid, C_5-alkene triols and 2-methyltetrols were estimated using the response factor of *meso*-erythritol [*Wang et al.,* 2008; *Kourtchev et al.*, 2008]. Meanwhile 3-methyl-1,2,3-butanetricarboxylic (MBTCA) and *β*-caryophyllinic acids were quantified using the response factors of pinic acid [*Jaoui et al.*, 2007], respectively. Target compounds were not detected in the field blank filters. The authentic standards or surrogates were spiked into precombusted quartz filters (*n* = 3), whose recoveries were 99±4.5% for *meso*-erythritol, 98±1.6% for *cis*-pinonic acid, 80±4.9% for pinic acid and 83±5.9% for 3-hydroxyglutaric acid. Relative standard deviations for the target compounds in duplicate samples were generally <10%.

4.3. Results and Discussion

4.3.1. OC, EC and WSOC concentrations

Concentrations of organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC) are summarized in Table 1. OC and EC concentrations were observed as 0.6-3.33 μg m^{-3} (ave. 1.73 μg m^{-3}) and 0.22-1.01 μg m^{-3} (0.42 μg m^{-3}), respectively. The concentration of WSOC ranged from 0.33 μg m^{-3} to 1.96 μg m^{-3} (0.92 μg m^{-3}). Relative abundance of WSOC in OC is on average 53.3%.

4.3.2. Secondary organic aerosol (SOA) tracers

Six isoprene-SOA tracers were identified in the Alaska aerosols, including 2-methylglyceric acid, three C_5-alkene triols, and two 2-methlytetrols (2-methylthreitol and 2-methylerythritol) (Table 1). The average concentrations of 2-methylthreitol and 2-methylerythritol were 3.78 ng m^{-3} and 9.86 ng m^{-3}, respectively. The values of 2-methyltetrols are higher than those reported from the Canadian High Arctic [*Fu et al.*, 2009], but lower than those reported in other sites of USA [*Ding et al.*, 2008]. The average concentration of three C_5-alkene triols (*cis*-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene and *trans*-2-methyl-1,3,4-trihydroxy-1-butene) were found to be 3.63 ng m^{-3}. The average concentration of 2-methylglyceric acid was 0.28 ng m^{-3}, which is higher than that reported in the Canadian High Arctic [*Fu et al.*, 2009] but lower than other previous studies from different sites of USA [*Cahill et al.*, 2006]. The measured values of isoprene-SOA tracers in this study are different than other sites may be due to different emission rates and meteorological conditions (temperature, intensity of solar radiation, relative humidity (RH) and the height of mixing layer, etc).

Four *α*-/*β*-pinene oxidation products such as *cis*-pinonic acid (PNA), pinic acid (PA), 3-hydroxyglutaric acid (HGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) were detected in this study. The average concentrations of PNA and PA were 2.16 and 3.96 ng m^{-3}, respectively. The levels of HGA and MBTCA were observed 0.41 and 1.52 ng m^{-3}, respectively. *Ding et al.* (2014) reported that MBTCA/HGA of *α*-pinene-SOA is higher than those of *β*-pinene- or *δ*-limonene-SOA. Thus, the ratio of HGA to MBTCA (HGA/MBTCA) can be used to determine the major precursors (*α*-pinene, *β*-pinene, etc.) for monoterpene-SOA. The value of HGA/MBTCA was lower in the southeastern U.S (~1.0) than California (1.8-3.6), indicating a major contribution from *α*-pinene to monoterpene-SOA in this area [*Lewandowski et al.*, 2013]. *α*-Pinene was the major precursor in Hefei and Qianyanzhou,

while the HGA/MBTCA ratios were 1.16 and 0.75, respectively [*Ding et al.*, 2014]. The lower ratio of HGA to MBTCA (0.93) was obtained in present study, suggesting that *α*-pinene was the major contributor for monoterpene-SOA in Alaska atmosphere.

Sesquiterpenes have been the little studied BVOCs due to their high reactivity and relatively low vapor pressure [*Duhl et al.*, 2008]. *β*-Caryophyllene is one of the most abundant species among the sesquiterpenes, whose oxidation products are also frequently reported [*Duhl et al.*, 2008]. *β*-Caryophyllinic acid can be formed by ozonolysis or photo-oxidation of *β*-caryophyllene [*Jaoui et al.*, 2007], which was detected in the Alaskan samples with average concentration of 1.53 ng m^{-3}. This value is also higher than that of the Canadian High Arctic aerosols [*Fu et al.*, 2009].

4.3.3. Temporal variations

Temporal variations of OC, EC and WSOC were characterized by two major peaks in late autumn to early winter and late spring to early summer (Fig. 2a-c). Figure 3 presents temporal variations of the secondary oxidation products. All the isoprene-SOA tracers such as 2-methylglyceric acid, C$_5$-alkene triols, 2-methylthreitol and 2-methylerythritol exhibited very similar temporal trends to each other (Fig. 3a-d). The chamber experiment proposed that 2-methylglyceric acid is mainly derived under high-NOx condition whereas 2-methyltetrols are formed under low NO$_x$ (or NO$_x$ free) condition [*Surratt et al.*, 2010]. Thus, the ratio of 2-methylglyceric acid to 2-methyltetrols (MGA/MTLs) revealed the impact of NOx on isoprene-SOA formation. The MGA/MTLs were found to be 0.02-5.2 (ave. 1.0) in this study, which is higher than those reported from different sites of southeastern U.S. (0.13-0.35) and California (0.89) [*Lewandowski et al.*, 2013]. Seasonal impacts of NO$_x$ in central Alaska are discussed in section 4.3.4. Moreover, relative humidity can also influence the formation of MGA and MTLs [*Ding et al.*, 2013]. 2-Methyltetrols showed strong correlation with C$_5$-alkene triols (r = 0.93, p < 0.001, Fig. 4a), indicating similar formation process [*Kourtchev et*

al., 2008]. *Surrat et al*. [2010] proposed different formation pathways for MTLs and MGA. A good correlation was also observed between MTLs and MGA (r = 0.88, p < 0.001, Fig. 4b), suggesting that their sources probably similar. We found a significant correlation between isoprene oxidation products and monoterpene oxidation products (r = 0.47, p < 0.05, Fig. 4c), indicating that their major portion might be emitted from same sources or source regions. It should be noted that excluding the outlier as shown in Figure 4c, isoprene SOA tracers showed more stronger correlation with monoterpene-SOA tracers (r = 0.69, p < 0.001).

α-/β-Pinene-SOA tracers such as *cis*-pinonic, pinic, 3-hydroxyglutaric acids and MBTCA showed different temporal variations with isoprene oxidation products (Fig. 3e-h). *Fu et al.* [2010] also proposed different temporal variation between isoprene and α-/β-pinene products from Mt. Tai, Central East China. PNA and PA are the first generation products of monoterpene-SOA, which can be further photo-degraded to high-generation products, e.g., MBTCA, HGA [*Ding et al.*, 2014]. The ratio of PNA plus PN to MBTCA (P/M) can be used to understand the aging of monoterpene-SOA, whereas high P/M ratio and low P/M ratio indicates relatively fresh and aged monoterpene-SOA, respectively [*Gomez-Gonzalez et al.*, 2012; *Ding et al.*, 2014]. *Ding et al*. [2014] reported that the monoterpene-SOA was relatively fresh over China when P/M ratios were 0.89-21.0 (7.00±6.02). The ratios of P/M from fresh chamber experiment were found 1.51-3.21 [*Offenberg et al.*, 2007]. In this study, we observed P/M ratios from 0.82 to 131 (ave. 12.9), indicating that monoterpene-SOA was relatively fresh in central Alaska.

Temporal variations of β-caryophyllene oxidation products; β-caryophyllinic acid, exhibited different trends with isoprene- and α-/β-pinene-SOA tracers (Fig. 3i). *Akagi et al.* [2011] reported that BVOCs could be emitted from biomass burning. In this study, β-caryophyllinic acid was dominantly observed in winter, showing similar temporal trends and significant correlation with levoglucosan (r = 0.65, p < 0.001, Fig. 4d), suggesting that β-

caryophyllinic acid are associated with biomass burning [*Fu et al.*, 2010]. During wintertime air masses mainly come from the Arctic Ocean and regional area (chapter 2, Fig. 2, 3) and there was no forest fire in this time. During this period, levoglucosan, EC and β-caryophyllinic acid showed higher concentrations, suggesting that β-caryophyllinic acid was more associated with regional biomass burning probably from domestic stoves. However, little is known about the source of sesquiterpene including β-caryophyllene from wheat straws, crop, other species, etc. [*Duhl et al.*, 2008; *Fu et al.*, 2010]. Due to low volatility of sesquiterpenes, they could be accumulated in leaves and woods and abundantly emitted by biomass burning [*Ciccioli et al.*, 2014]. However, to our knowledge there is no report on β-caryophyllinic acid from wood burning during cold season. *Yttri et al.* [2014] reported that the Arctic bordering countries, i.e., Scandinavian countries, Canada, USA, and Russia, are familiar with usages of substantial amounts of wood for residential heating. Thus, the burning of wood or agricultural wastes could be a source of sesquiterpenes such as β-caryophyllene to produce β-caryophyllinic acid. In contrast, no correlations were observed between levoglucosan and isoprene-SOA tracers (r = -0.18, p = 0.32) or α-/β-pinene-SOA tracers (r = -0.42, p = 0.02), indicating that their emission sources are not similar and emissions of isoprene/monoterpene from forest fire are not important.

4.3.4. Seasonal variations

Concentrations of isoprene-SOA tracers ranged from 0.02 to 16.6 ng m^{-3} (ave. 4.14 ng m^{-3}) whereas highest level was observed in summer (8.77 ng m^{-3}) followed by spring (2.41 ng m^{-3}), autumn (0.18 ng m^{-3}) and winter (0.04 ng m^{-3}) (Fig. 5a). The MGA/MLTs ratios showed clear seasonal trend with winter maximum (3.0) and summer minimum (0.03), suggesting impact of NOx in the formation of isoprene-SOA in Alaska aerosol. Among these isoprene-SOA tracers, 2-methyltetrols were most abundant in all seasons, except for winter (Table 1). Previous studies also proposed that the low NOx product, MTLs are dominant among

isoprene-SOA tracers in most cases, especially in summer period [*Ding et al.*, 2013; *Fu et al.*, 2010; *Lewandowski et al.*, 2007]. 2-Methyltetrols showed the highest value in summer (14.5 ng m^{-3}) while MGA/MLTs ratio was lowest in summer. In contrast, 2-methylglyceric acid exhibited higher value than 2-methyltetrols and C$_5$-alkene triols in winter (Table 1), whereas MGA/MLTs ratio was highest in winter, suggesting high NO$_x$ condition due to the more burning activities.

Higher SOA yields from isoprene also indicate low NOx conditions in summertime [*Kroll et al.*, 2006]. However, low concentrations were observed for isoprene-SOA tracers in wintertime due to the less emission of isoprene. As shown in Fig. 5b, the isoprene oxidation products exhibited significant seasonal difference. All the isoprene SOA-tracers showed higher concentrations in summer than any other seasons. The seasonal variations of isoprene-SOA tracers might be affected by several factors such as emission, reaction rates and meteorological conditions including NOx concentration, temperature, solar radiation, relative humidity, etc. The higher emission of isoprene from surrounding boreal black spruce forest in summer, when light intensity and ambient temperature are enhanced, supports an intensive production of isoprene-SOA tracers in the boreal atmosphere [*Ding et al.*, 2012]. Concentrations of *α-/β*-pinene-SOA tracers ranged from 0.42-8.24 ng m^{-3} (ave. 2.01 ng m^{-3}). Highest concentration of *α-/β*-pinene-SOA tracers was found in spring (3.55 ng m^{-3}) followed by summer (2.40 ng m^{-3}), autumn (0.73 ng m^{-3}) and winter (0.56 ng m^{-3}) (Fig. 5a). *Kim* [2001] proposed that due to the influence of bud formation and elongation, emission rates for terpenes could be the highest in spring than other seasons in the southeastern U.S. During spring, *cis*-pinonic acid was the dominant species (ave. 6.26 ng m^{-3}) among all of *α-/β*-pinene-SOA traces, followed by pinic acid (5.97 ng m^{-3}), MBTCA (1.60 ng m^{-3}) and 3-hydroxyglutaric acid (0.37 ng m^{-3}). *Ding et al*. [2008] also reported high level of *cis*-pinonic acid in early spring from Alabama, southeastern United States. In contrast, pinic acid was the

abundant compound (ave. 5.18 ng m^{-3}) in summer, followed by MBTCA (2.65 ng m^{-3}), *cis*-pinonic acid (1.34 ng m^{-3}) and 3-hydroxyglutaric acid (0.59 ng m^{-3}). The emission and reaction rates of *α-/β*-pinene should be also significant in summer due to high temperature and intense solar radiation [*Zheng et al.*, 2010]. 3-Hydroxyglutaric acid exhibited lower concentration in all seasons without any significant seasonal variation (Fig. 5c). The P/M ratios were higher in spring (ave. 28.4) and winter (21.0) compared to autumn (9.9) and summer (3.3), indicating that monoterpene-SOA were more fresh in spring and winter.

Interestingly, *β*-caryophyllene-SOA tracer (e.g., *β*-caryophyllinic acid) showed different seasonal trend than isoprene- and *α-/β*-pinene-SOA tracers (Fig. 5a). *β*-Caryophyllinic acid exhibited the highest value in winter (ave. 4.04 ng m^{-3}), followed by autumn (2.10 ng m^{-3}), spring (0.85 ng m^{-3}) and summer (0.62 ng m^{-3}). As already mentioned in section 4.3.3, *β*-caryophyllinic acid showed similar trend with levoglucosan, suggesting that it might be associated with emissions of biomass burning products.

4.3.5. Contributions of isoprene, α-/β-pinene- and β-caryophyllene-SOA tracers to OC and WSOC

Contributions of isoprene-SOA tracers to OC (0.003-1.9%, ave. 0.56%) and WSOC (0.005-4.2%, 1.2%) are higher than those of *α-/β*-pinene- (0.04-2.1%, 0.31% and 0.01-2.1%, 0.55%, respectively) and *β*-caryophyllene-SOA tracer (0.003-0.29%, 0.06% and 0.01-0.37%, 0.11%, respectively). The contributions of isoprene oxidation products to OC were found to be highest in summer (1.2%) followed by spring (0.25%), autumn (0.05%) and winter (0.01%) (Fig. 6a). In contrast, contributions of *α-/β*-pinene oxidation products to OC showed highest value in spring (0.63%) followed by summer (0.31%), autumn (0.14%) and winter (0.08%) (Fig. 6a). On the other hand, those of *β*-caryophyllene-SOA tracer exhibited highest level in winter (0.15%), followed by autumn (0.08%), spring (0.05%) and summer (0.02%).

In addition, contributions of the SOA tracers to WSOC showed seasonal variation similar to the contribution of SOA tracers to OC (Table 1, Fig. 6b).

4.3.6. Contributions of isoprene, α-/β-pinene and β-caryophyllene to secondary organic carbon (SOC)

Contributions of BVOCs to SOC were estimated using a tracer-based method proposed by *Kleindienst et al.* [2007]. Based on chamber experiments, the aerosol mass fraction (f_{soa}) is defined as

$$f_{soa} = \frac{\sum_i [\text{tr}i]}{[\text{SOA}]}$$

where [tr$i$] is the concentration of the tracer, i, in ng m^{-3} and [SOA] is the mass concentration of SOA. Using the measured concentrations of SOA tracers in this study and the laboratory-derived tracer mass fraction (f_{soc}) factors of 0.155 ± 0.039 for isoprene, 0.231 ± 0.111 for α-pinene and 0.0230 ± 0.0046 for *β*-caryophyllene [*Kleindienst et al.*, 2007], we calculated the contributions of SOA products to SOC (Table 2). *Kleindienst et al.* [2007] proposed standard deviations for the laboratory-generated mass fraction, 25% for isoprene, 48% for α-pinene and 22% for *β*-caryophyllene. However, other systematic error also may be present in the study [*Kleindienst et al.*, 2007]. The main systematic error is probably caused from the different conditions (relative humidity, precursor concentrations and particulate matter concentration) of chamber experiments compared to those in the ambient atmosphere. Further, the mass fractions of SOA generated from the chamber experiments might be different from the ambient aerosols. The time of chamber processing is also different (usually less) than that occurring in the ambient atmosphere. There is some uncertainty associated for the estimation of SOC by using SOA-tracer method due to the surrogate standards. Though, the tracer-based method is widely used to estimate SOC [*Stone et al.*, 2009; *Lewandowski et al.*, 2013].

The contributions of BVOCs (isoprene, α-/β-pinene and β-caryophyllene) to SOC were estimated 55-844 ngC m^{-3} (ave. 261 ngC m^{-3}), accounting for 4.7-33.6% (14.4%) of OC, in which isoprene is the dominant contributor (159 ngC m^{-3}; 8.0%) followed by α-/β-pinene (35 ngC m^{-3}; 2.3%) and β-caryophyllene (66.3 ngC m^{-3}; 4.1%) (Fig.7a). The unexplained OC might come from other primary sources including biomass burning tracers and other organic compounds. The isoprene SOC showed the highest value in summer (338 ngC m^{-3}) followed by spring (93 ngC m^{-3}), autumn (6.87 ngC m^{-3}) and winter (1.46 ngC m^{-3}). The contributions of isoprene-SOC to OC were obtained to be 11-27.3% (17.4%) for summer, 0.09-12.1% (3.7%) for spring, 0.04-3.1% (0.66%) for autumn and 0.05-0.15% (0.08%) for winter (Fig. 7b). In contrast, α-/β-pinene-SOC exhibited the largest value in spring (ave. 61.7 ngC m^{-3}) followed by summer (42.4 ngC m^{-3}), autumn (12.6 ngC m^{-3}) and winter (9.8 ngC m^{-3}) whereas β-caryophyllene-SOC showed the maximum in winter (175 ngC m^{-3}) followed by autumn (91.2 ngC m^{-3}), spring (36.8 ngC m^{-3}) and summer (26.8 ngC m^{-3}). Contributions of α-/β-pinene and β-caryophyllene SOC to OC were calculated to be 0.98-4.7% (2.5%) and 0.23-2.3% (1.4%) in summer, 0.31-2.3% (1.1%) and 2.6-7.6% (5.6%) in autumn, 0.34-1.4% (0.63%) and 5.5-19.5% (9.6%) in winter, 2.0-14.1% (4.5%) and 0.79-7.7% (3.5%) in spring, respectively.

Among these tracers, estimated SOC from different precursors demonstrates that over 81% of the estimated SOC were from isoprene precursor in summer whereas α-/β-pinene and β-caryophyllene revealed highest contribution in spring (39%) and winter (92%), respectively. *Fu et al.* [2009] reported that isoprene was the largest SOC contributor in the Canadian High Arctic aerosols in early June when the air masses mainly come from North America. *Kleindienst et al.* [2007] also proposed that isoprene was the dominant contributor in the summer aerosols collected at Research Triangle Park, NC. Same set of isoprene-SOA traces and β-caryophyllinic acid, whereas only four among the nine monoterpene-SOA

tracers   reported by *Kleindienst et al.* [2007] were used for SOC and SOA estimations in this study. Thus, the current result for monoterpene-SOC should underestimate due to the mismatch of tracer compositions. *Wang et al.* [2013] also proposed significant underestimation of monoterpene-SOC caused by using mismatch tracer compositions.

4.4. Summary

In the present study, biogenic SOA tracers of isoprene (2-methylglyceric acid, C_5-alkene triols and 2-methyltetrols), α-/β-pinene (pinonic acid, pinic acid, 3-hydroxyglutaric acid and MBTCA) and β-caryophyllene (β-caryophyllinic acid) were identified in the ambient aerosols from central Alaska, USA. Isoprene-SOA tracers exhibited higher concentrations in summer (ave. 8.77 ng m^{-3}), whereas α-/β-pinene- and β-caryophyllene-SOA tracers showed the highest values in spring (3.55 ng m^{-3}) and winter (4.04 ng m^{-3}), respectively. Their total amounts account for 0.13-2.5% (0.92%) of organic carbon (OC) and 0.17-5.6% (1.9%) of water-soluble organic carbon (WSOC) during the study period. Isoprene- and α-/β-pinene-SOA tracers showed higher levels in summer and spring while β-caryophyllene-SOA tracer revealed higher value in winter. Interestingly, β-caryophyllinic acid exhibited similar temporal pattern with levoglucosan whereas highest level of β-caryophyllinic acid was observed in winter, assuming that β-Caryophyllinic acid could be originated from wood burning (e.g., residential heating). Higher contributions of isoprene-SOA tracers to SOA formation in summer probably due to the larger isoprene emissions and relatively high levels of oxidants (e.g., OH).

The contributions of isoprene, α-/β-pinene and β-caryophyllene to SOC formation were estimated using tracer-based method. The estimated isoprene-derived SOC is about 5 times higher than α-/β-pinene-derived SOC and 2 times higher than β-caryophyllene-SOC. From air mass back trajectory, we observed mixed air masses in all seasons with short distances (chapter 2, Fig. 2, 3), suggesting that Alaska boreal black spruce forest and tundra

could be the major sources of isoprene and *α-/β*-pinene-SOA. We found that estimated concentrations of *β*-caryophyllene-derived SOC maximized in winter and *β*-caryophyllene-SOC to OC ratio also peaked in winter. Local biomass burning from residential heating with wood stoves in winter and *β*-caryophyllene-SOC may be the main source of *β*-caryophyllinic acid. Based on measured SOA tracers, this study suggests that isoprene is a more important precursor for the production of biogenic SOA than *α-/β*-pinene and *β*-caryophyllene in subarctic Alaska, but emphasizes that sesquiterpene derived from residential biomass burning significantly contributes to the SOA formation in winter.

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Table 1

Average concentrations of OC, EC, WSOC ($\mu g\ m^{-3}$) and biogenic SOA tracers (ng m^{-3}) measured in the Alaska Aerosols.

| Species	summer			autumn			winter			spring		
	avg[a]	min	max	avg	min	max	avg	min	max	avg	min	max
OC	1.86	1.10	3.32	1.63	0.76	2.77	1.87	0.95	2.96	1.49	0.60	3.33
EC	0.31	0.22	0.40	0.54	0.30	1.01	0.54	0.30	0.85	0.40	0.22	0.70
WSOC	0.84	0.39	1.7	0.95	0.37	2.0	1.13	0.58	1.7	0.90	0.33	1.8
isoprene SOA tracers												
2-methylglyceric acid	0.5	0.11	1.2	0.06	0.04	0.08	0.09	0.04	0.20	0.23	0.04	0.73
ΣC_5-alkene triols[b]	7.7	3.1	18.5	0.16	0.01	0.73	0.02	0.01	0.03	2.13	0.01	10.2
2-methylthreitol	7.8	2.7	19.1	0.14	0.00	0.59	0.04	0.01	0.14	2.7	0.01	10.3
2-methylerythritol	21.2	7.4	46.6	0.42	0.02	2.1	0.04	0.02	0.10	5.2	0.02	21.1
total isoprene SOA products (mean)	8.77	0.5	21.2	0.18	0.05	0.42	0.04	0.01	0.09	2.41	0.22	5.2
% of OC	1.2	0.76	1.9	0.05	0.00	0.21	0.01	0.00	0.01	0.25	0.01	0.84
% of WSOC	2.75	1.6	4.2	0.10	0.00	0.49	0.01	0.01	0.01	0.45	0.01	1.5
α-/β-pinene SOA tracers												
3-hydroxyglutaric acid	0.59	0.21	1.1	0.23	0.15	0.31	0.23	0.14	0.54	0.37	0.11	1.2
cis-pinonic acid	1.34	0.17	5.2	0.65	0.23	1.3	0.68	0.31	1.1	6.26	1.7	25.3
pinic acid	5.18	1.8	13	1.7	0.7	3.7	1.3	0.48	1.8	5.97	1.3	16.6
MBTCA[c]	2.65	0.95	4.8	0.38	0.1	1.3	0.1	0.06	0.15	1.6	0.21	6.7
total α-/β-pinene SOA products (mean)	2.4	0.59	5.2	0.73	0.21	1.7	0.56	0.1	1.2	3.55	0.37	6.3
% of OC	0.31	0.11	0.61	0.14	0.04	0.29	0.08	0.04	0.19	0.63	0.27	2.1
% of WSOC	0.72	0.24	1.5	0.27	0.06	0.68	0.14	0.08	0.31	0.89	0.38	2.1
β-caryophyllene SOA tracers												
β-caryophyllinic acid	0.62	0.10	1.7	2.1	0.62	3.3	4.04	2.0	9.0	0.85	0.18	1.3
% of OC	0.02	0.00	0.03	0.08	0.04	0.12	0.15	0.08	0.29	0.05	0.01	0.12
% of WSOC	0.05	0.01	0.09	0.15	0.09	0.22	0.23	0.14	0.37	0.09	0.01	0.16

[a]avg :average.
[b] C$_5$-alkene triols: *cis*-2-methyl-1,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene and 3-methyl-2,3,4-trihydroxy-1-butene.
[c]MBTCA; 3-methyl-1,2,3- butanetricarboxylic acid.

1

Table 2

Contributions of SOA precursors to SOC estimated using a tracer-based method [*Kleindienst et al.*, 2007].

Species	summer			autumn			winter			spring		
	avg[a]	min	max	avg	min	max	avg	min	max	avg	min	max
isoprene SOA tracers												
SOC (ngC m^{-3})	338	128	718	6.87	0.74	31.9	1.46	0.66	3.1	93	0.69	402
% of SOC	81	61.4	89.3	8.5	0.54	38.5	0.81	0.59	1.3	24.4	0.96	71.6
% of OC	17.4	11	27.3	0.66	0.04	3.1	0.08	0.05	0.15	3.7	0.09	12.1
α-/β-pinene SOA tracers												
SOC (ngC m^{-3})	42.4	21.6	88.7	12.6	7.4	24	9.8	7.8	13.1	61.7	14.6	143.2
% of SOC	11.8	5.5	25.9	13.7	5.4	29	6.8	2.3	11.9	39.1	18.3	82.8
% of OC	2.5	0.98	4.7	1.1	0.31	2.3	0.63	0.34	1.4	4.5	2	14.1
β-caryophyllene SOA tracers												
SOC (ngC m^{-3})	26.8	4.5	74.6	91.2	26.9	144	175	87.8	391	36.8	8	57
% of SOC	7.2	1.4	13.1	77.8	32.5	94.1	92.4	87.5	96.9	36.6	4.6	78.9
% of OC	1.4	0.23	2.3	5.6	2.6	7.6	9.6	5.5	19.4	3.5	0.79	7.7
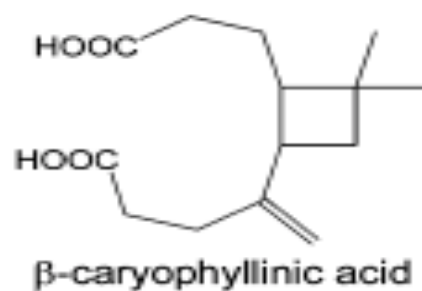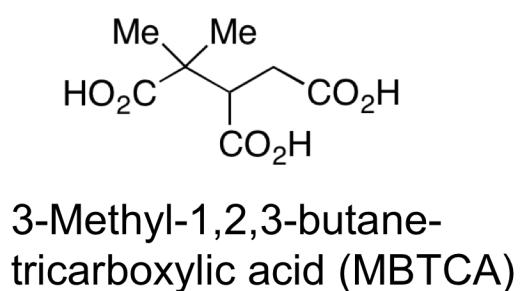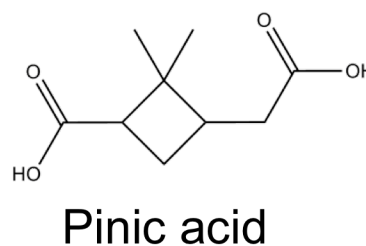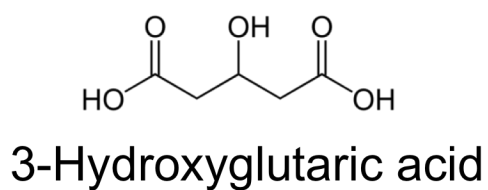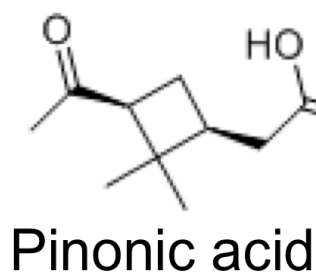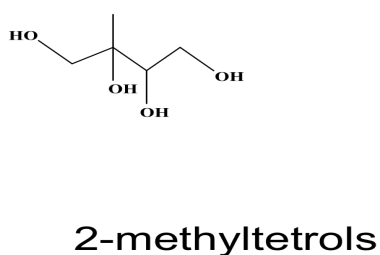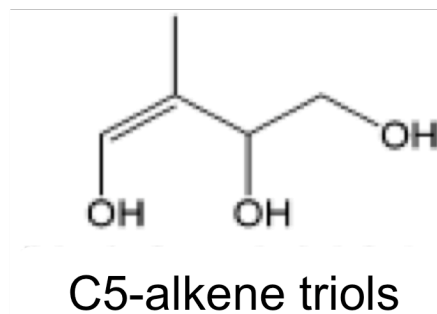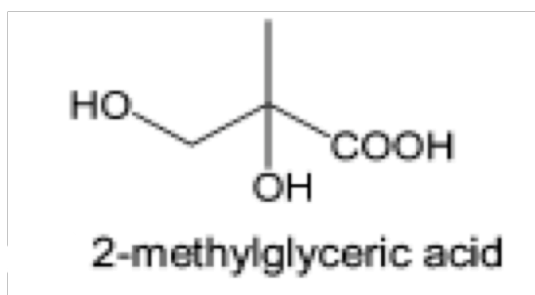
Fig. 1. Chemical structures of identified biogenic SOA tracers in Alaska aerosols.
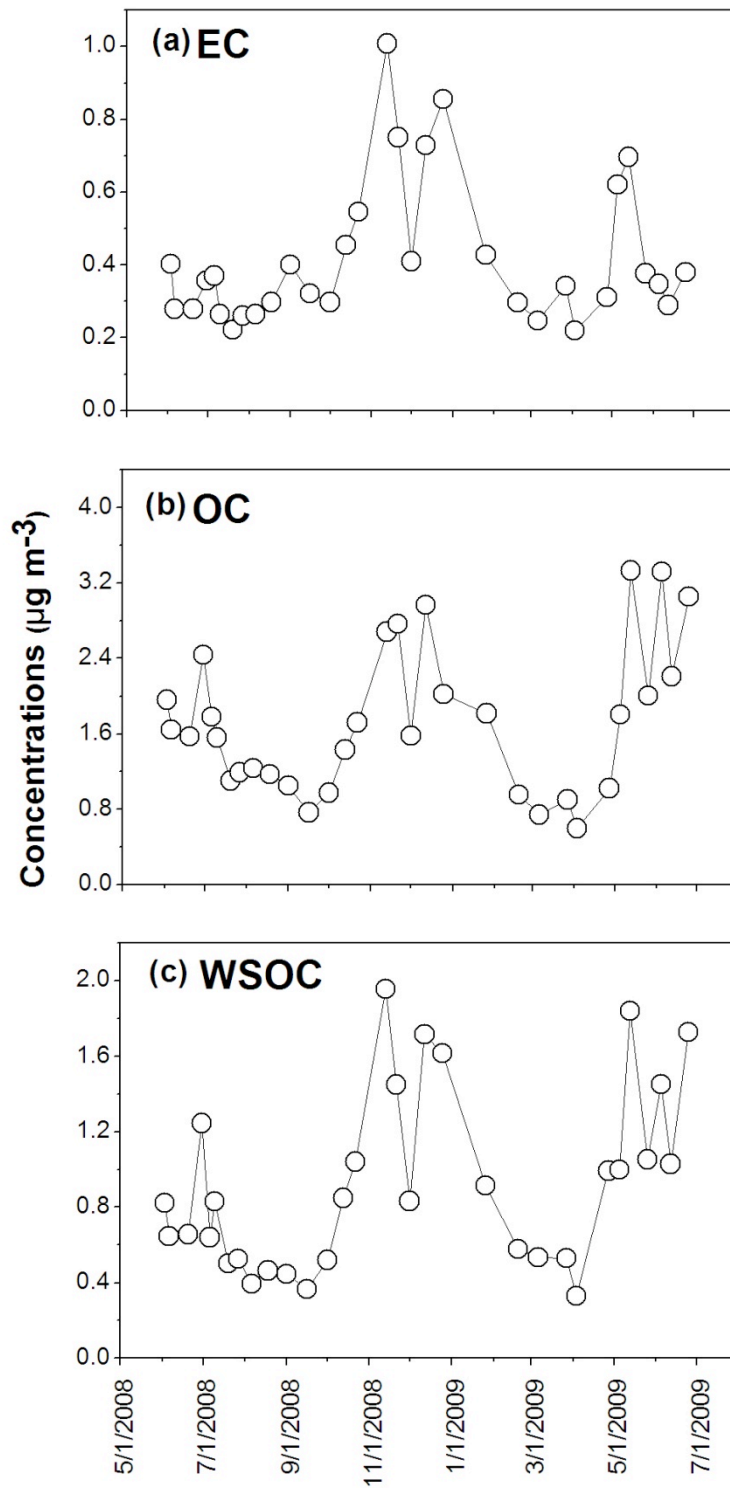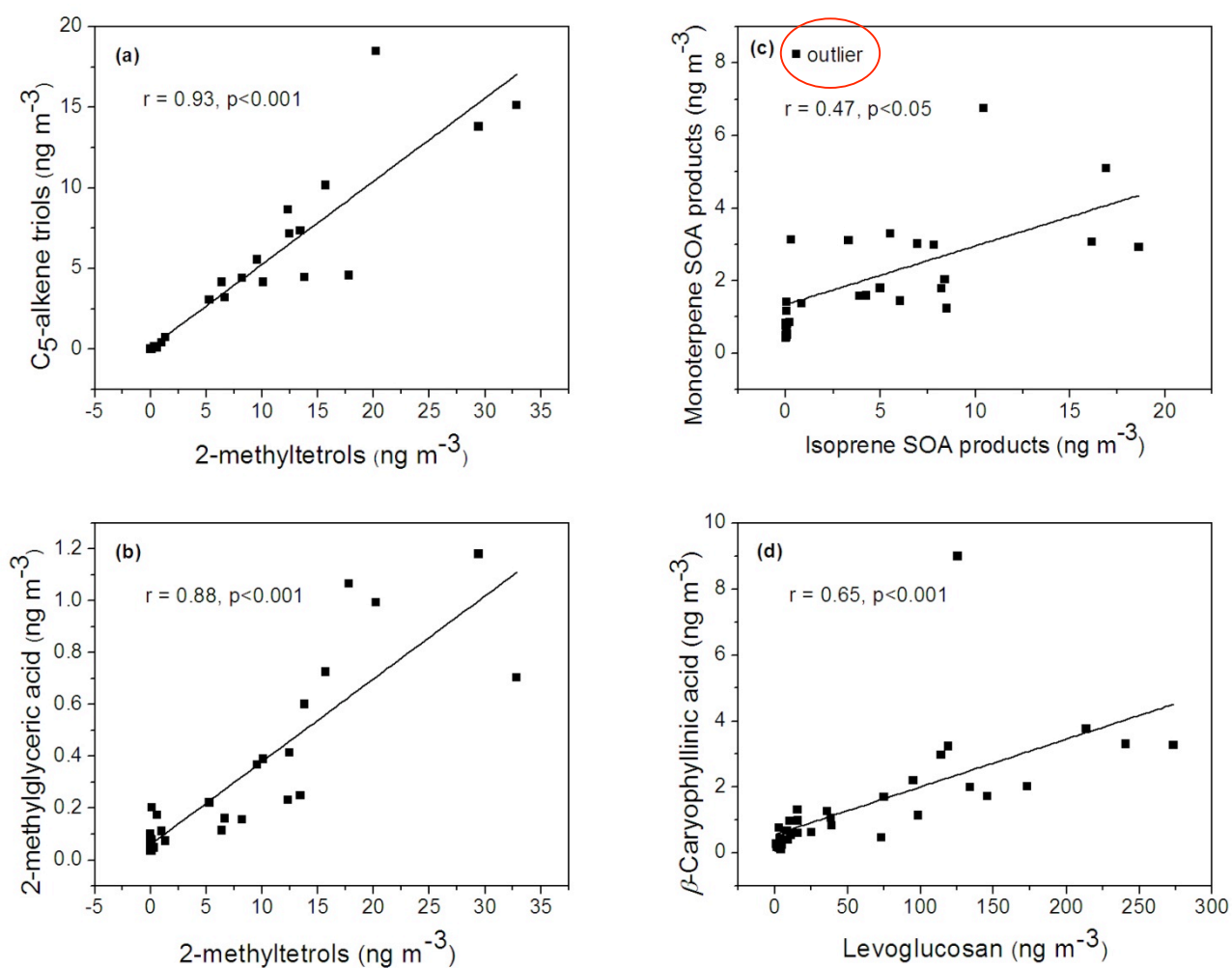
Fig. 2. Temporal variations of (a) EC, (b) OC, and (c) WSOC in the Alaskan aerosols.
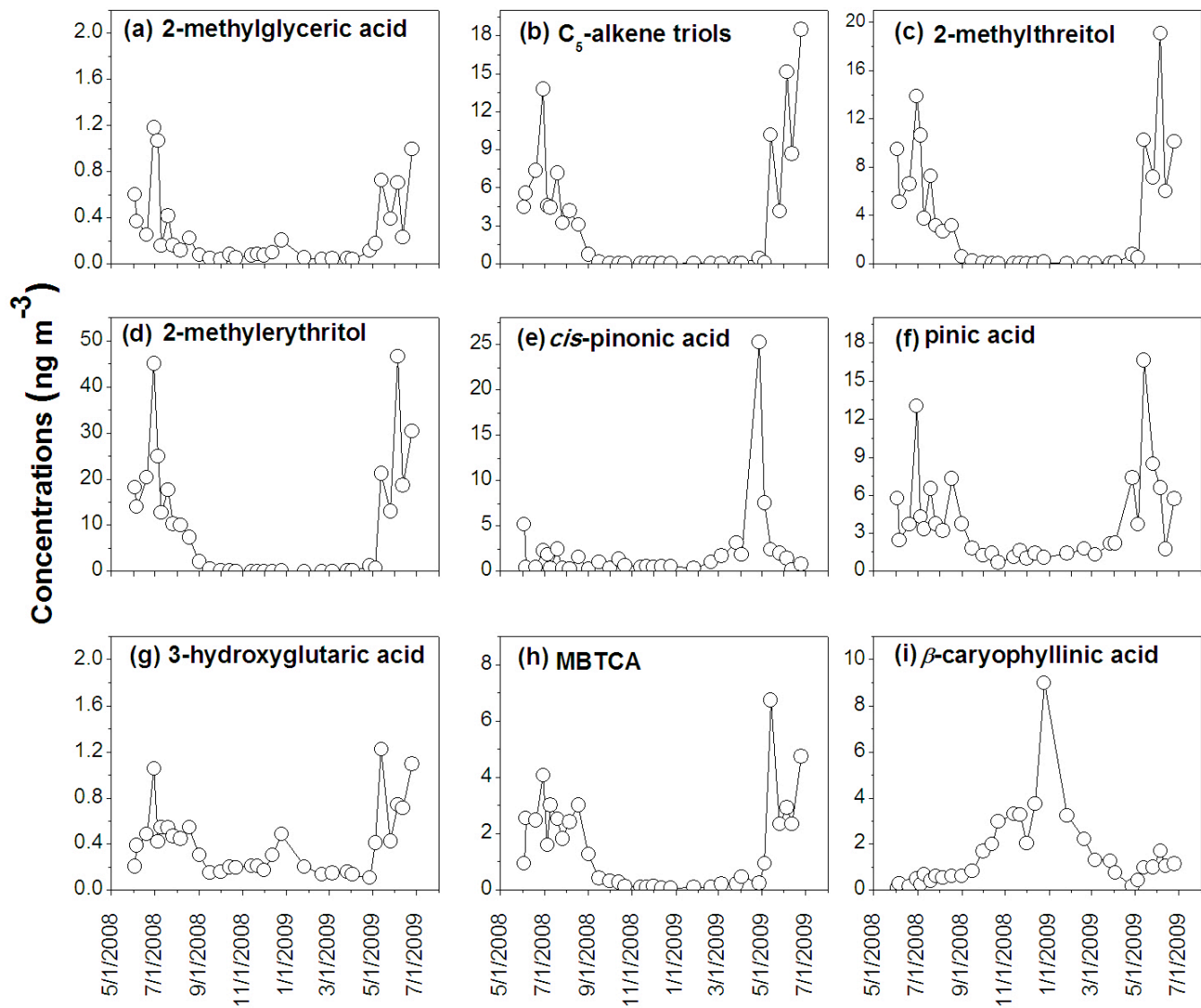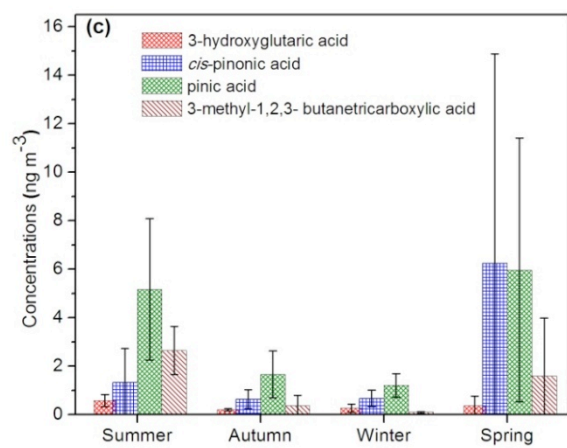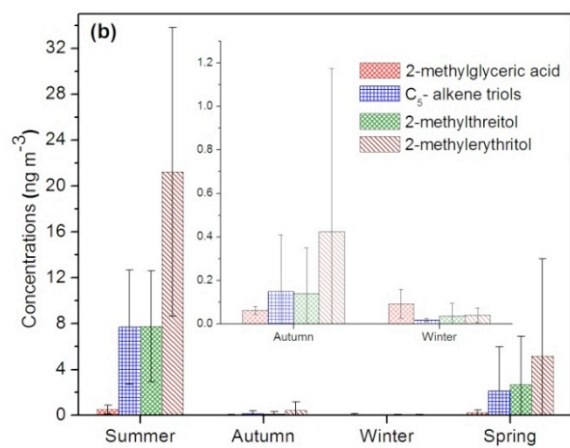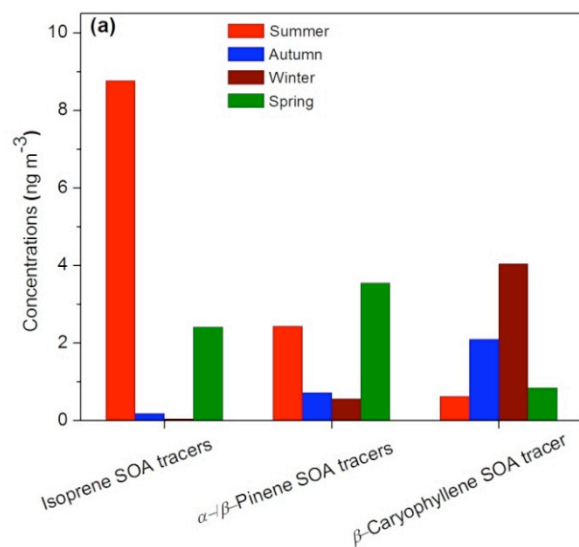
Fig. 3. Temporal variations of biogenic SOA tracers measured in the Alaskan aerosols.

Fig. 4. Relations between (a) C_5-alkene triols and 2-methyltetrols, (b) 2-methylglyceric acid and 2-methyltetrols, (c) monoterpene SOA products and isoprene SOA products, and (d) β–caryophyllinic acid and levoglucosan.

Fig. 5. Seasonal variations of (a) isoprene, α-/β-pinene and β-caryophyllene SOA tracers, (b) isoprene SOA tracers, and (c) α-/β-pinene SOA traces.
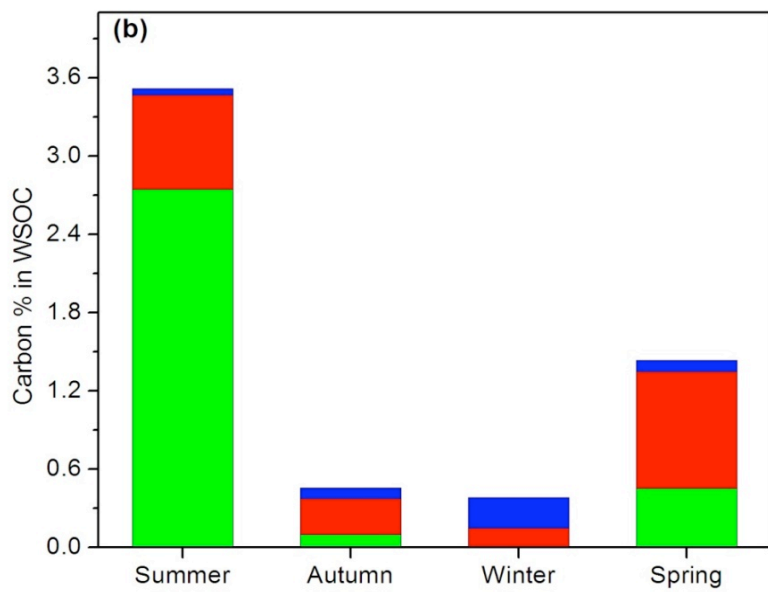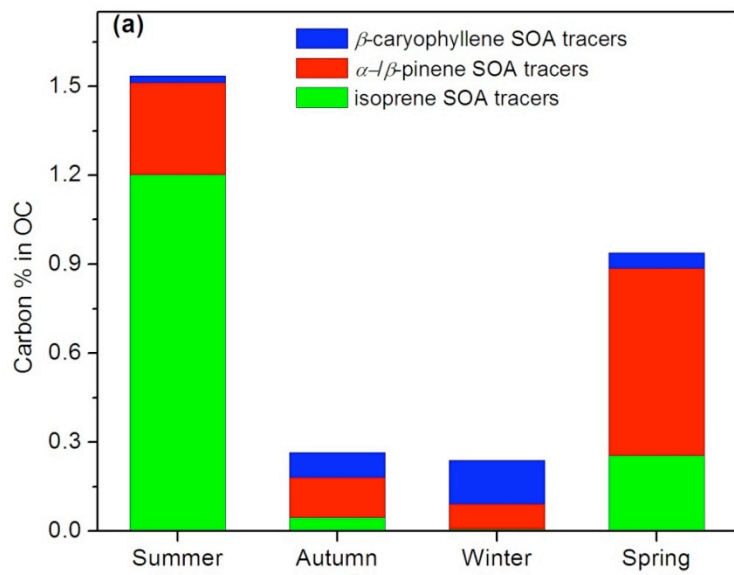
Fig. 6. Contributions (%) of biogenic SOA tracers to (a) OC and (b) WSOC.
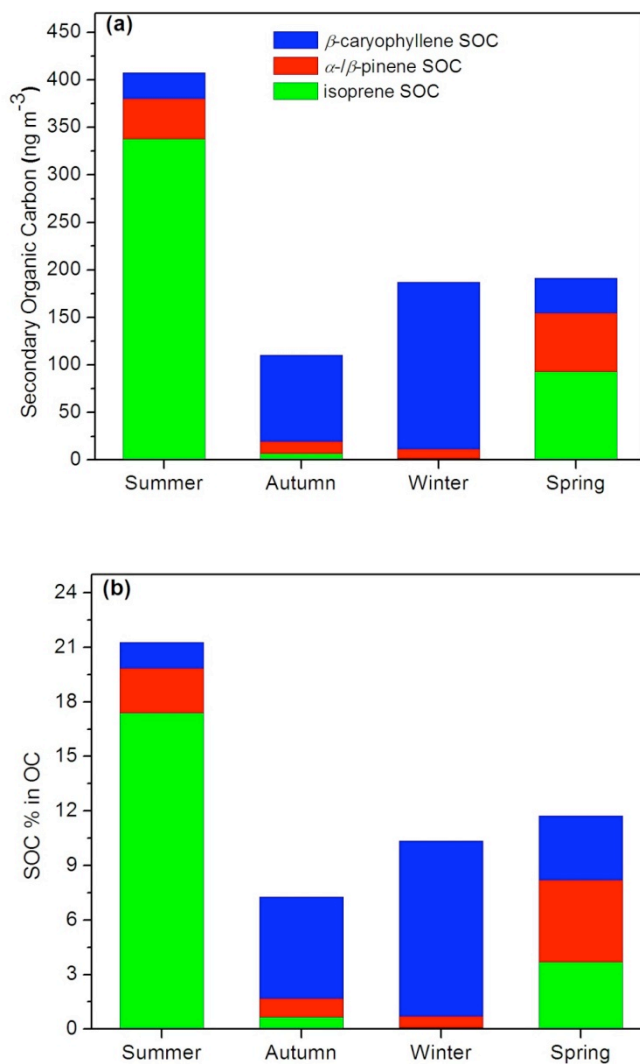
Fig. 7. (a) Carbon concentrations of isoprene-, *α-/β*-pinene- and *β*-caryophyllene-derived SOC and (b) contributions (%) of SOC to ambient OC.

Chapter 5: Characterization of primary biological aerosol particles (PBAPs) in ambient aerosols of Alaska

5.1. Introduction

Organic aerosols are highlighted for the past decade due to their importance of environmental issues related to global and regional climate, chemistry of the atmosphere, biogeochemical cycling, and people's health [*Crutzen and Andreae,* 1990; *Kanakidou et al.,* 2005; *P¨oschl*, 2005; *Andreae and Rosenfeld*, 2008]. Water-soluble organic compounds (WSOC) account for 11–95% of organic carbon (OC) [*Mader et al.,* 2004] which is highly active in altering the cloud condensation nucleui (CCN) activity of the particles, affecting radiative forcing and climate [*Decesari et al.,* 2006; *Martin et al.,* 2010]. Sugars are an important part of water-soluble organic compounds, whose concentrations are substantial in atmospheric aerosol over the continental [*Graham et al.,* 2003; *Decesari et al.,* 2006; *Medeiros et al.,* 2006; *Wan and Yu*, 2007; *Yttri et al.,* 2007; *Fu et al.,* 2008; *Jia and Fraser*, 2011], marine [*Simoneit et al.,* 2004; *Fu et al.,* 2011] and high Arctic regions [*Fu et al.,* 2009]. Sugars can account for 0.5-10% of carbon in atmospheric particulate matter, can be used as tracers for primary biological aerosol particles [*Graham et al.,* 2003; *Medeiros et al.,* 2006; *Yttri et al.,* 2007; *Fu et al.,* 2013].

Primary biological aerosol particles (PBAP), including pollen, bacteria, fungal and fern spores, viruses, algae, and fragments of plants and animals, contribute substantially to primary organic aerosol (POA) [*Despres et al.,* 2012; *O'dowd et al.,* 2004; *Yttri et al.,* 2007]. Previous studies demonstrated the influence of PBAPs to the clouds and precipitation [*Huffman et al.,* 2013; *Pöschl et al.,* 2010; *Prenni et al.,* 2009], which is favored by laboratory studies for PBAPs, acting directly as CCN and ice nuclei (IN) [*Haga et al.,* 2013; *Morris et al.,* 2013; *Pummer et al.,* 2012].

Primary sugars consist of glucose, fructose, sucrose, trehalose, and xylose are emitted persistently from biological sources and have been considered as tracers for PBAP [*Medeiros et al.*, 2006; *Pacini*, 2000]. Fructose and glucose have been proposed as tracers from biogenic sources such as terrestrial plant pollen, fruits, and detritus [*Speranza et al.*, 1997]. Glucose exists as the most abundant carbohydrate in vascular plants [*Cowie and Hedges*, 1984]. Sucrose is the dominant sugar component of airborne pollen grains [*Fu et al.*, 2012a; *Pacini*, 2000; *Yttri et al.*, 2007] which plays an important role in plant flowering processes [*Bieleski*, 1995]. Trehalose is well known as a fungal metabolite which is frequently accompanied by the resuspension of soil particles and unpaved road dust [*Rogge et al.*, 2007; *Simoneit et al.*, 2004a]. In contrast, xylose is a monosaccharide exist broadly in the plants, can be emitted from biomass burning of plant materials [*Sullivian et al.*, 2011].

Sugar alcohols such as arabitol, manitol, inositol, and erythritol have also been used as tracers for PBAP [*Graham et al.*, 2003, *Simoniet et al.*, 2004b; *Fu et al.*, 2010]. Arabitol and mannitol are the major metabolites in microorganism, especially in fungi [*Di Filippo et al.*, 2013; *Velez et al.*, 2007] and they have been proposed as tracers for fungal spores [*Bauer et al.*, 2008; *Jia and Fraser*, 2011; *Yang et al.*, 2012]. Recent study reported that erythritol and inositol also emit from similar sources like as other sugar alcohols such as arabitol and mannitol [*Chen et al.*, 2013]. It should be noted that sugar compounds (e.g., erythritol, arabitol, maltose etc.) can further be emitted from biomass burning [*Medeiros et al.*, 2008].

Boreal forest account for about one-third of the carbon sequestered in terrestrial ecosystem which is located in the high latitudes including Alaska, Canada, Russia and Northern Europe. The boreal and tundra forest ecosystem can release large amount of biogenic organic tracers in the atmosphere. Moreover, microbial activity between the atmosphere and forest soils is

enhanced due to the high temperature in hot season, especially during forest fire occurring [*Kim et al.*, 2003]. As a result, substantial PBAPs can be emitted in the Alaska atmosphere from soil microbes during summer and spring. The purpose of this study is to investigate the abundances of primary sugars and sugar alcohols, in order to address the influence of PBAP, their seasonal variations and sources in ambient aerosols form interior Alaska.

5.2. Experimental

5.2.1. Extraction and Derivatization

The extraction process has been discussed in chapter 2.

5.2.2. Compound Identification

The sugar compounds were identified by using gas chromatography-mass spectrometry GC-MS) technique (see chapter 2). The mass fragmentation ions pattern of m/z = 217/204/191, 217/204/437 and 217/204/361 were used for the quantification of glucose & xylose, fructose, and sucrose & trehalose, respectively. Moreover, mass fragmentation ions of m/z = 217/205, 217/205/307/319 and 217/204/305/318 were used for erythritol, arabitol & mannitol, inositol, respectively. Recoveries of the major compounds were more than 75%. The data reported here were not corrected for recoveries.

5.3. Results and Discussion

5.3.1. Ambient concentrations

5.3.1.1. Concentrations of primary sugars in ambient aerosol

Five primary sugars such as glucose, fructose, sucrose, trehalose, and xylose, were detected in the aerosols from Alaska (Fig 1). The average concentrations of primary sugars were 1.18-

30.5 ng m^{-3}. They are derived from various sources including microorganism, plants and animals [*Simoneit et al.*, 2004a]. The concentrations of glucose, fructose, sucrose, trehalose, and xylose were obtained in the range of 0.13-46.6 ng m^{-3} (average 12.0 ng m^{-3}), 0.06-14.7 (2.99 ng m^{-3}), 0.02-364 ng m^{-3} (30.5 ng m^{-3}), 0.03-14.3 ng m^{-3} (4.11 ng m^{-3}), and 0.03-7.48 ng m^{-3} (1.18 ng m^{-3}), respectively. Sucrose was the most abundant primary sugar, reaching a maximum concentration of 364 ng m^{-3}, which is higher than those reported in the high Arctic aerosols collected in winter to spring [*Fu et al.*, 2009]. The average concentrations of sucrose were up to 2-10 times higher than that of glucose, trehalose, and fructose, while xylose was present in the aerosols in low concentration level. The temporal plots of primary sugars are shown in Fig. 3.

Glucose was quantified as second abundant component in this study, which is the most common primary sugar synthesized in leaves during photosynthesis and stored in root stem flower and fruit in the plants [*Pacini et al.*, 2000]. Fructose showed significant correlation with sucrose (r = 0.79, p < 0.001), suggesting similar sources for both of them from growing plants, pollen, etc. Trehalose is a non-reducing disaccharide of glucose that plays an important physiological role in the stabilization of biological structures in a large number of organisms such as fungi, bacteria, and yeast [*Grag et al.*, 2002], and a few higher plants and invertebrates [*Medeiros et al.*, 2006a]. Trehalose is also considered to trace the resuspension of surface soil and unpaved road dust [*Simoneit et al.*, 2004b]. However, there is no good correlation between trehalose and tracer of soil dust e.g. nss-Ca^{2+} (r = 0.21, p = 0.22) in this study, indicating that trehalose mainly derived from terrestrial microbes or plant materials.

5.3.1.2. Concentrations of sugar alcohols in ambient aerosol

Arabitol, manitol, inositol, and erythritol are known as sugar alcohols, were identified in ambient aerosols of Alaska (Fig. 2). The average concentrations of sugar alcohols were observed

ranged from 0.38 to 17.0 ng m^{-3}. The concentrations of arabitol, manitol, inositol, and erythritol were found to be 0.09-89.7 ng m^{-3} (average 15.7 ng m^{-3}), 0.06-116 ng m^{-3} (17.0 ng m^{-3}), 0.01-1.47 ng m^{-3} (0.38 ng m^{-3}), and 0.10-11.9 ng m^{-3} (1.82 ng m^{-3}), respectively. The arabitol and manitol was detected as the major contributor to sugar alcohols in this study, which are used to tracer for numerous microorganism including fungi, bacteria, algae, etc. [*Bauer et al.*, 2008; *Pashanska et al.*, 2002;]. *Yttri et al.*, [2007] also reported that arabitol and manitol were most abundant species among the all sugar-alcohols in the aerosol samples collected from different background site in Norway. The concentrations level of sugar alcohols in Alaska is higher than Canadian high Arctic aerosols [*Fu et al.*, 2009]. The time series of individual sugar alcohols are presented in Fig. 5, which clearly indicate the large variation during the study period. All sugar alcohols except erythritol showed similar temporal trends, whereas large peaks were observed from May-August.

Different fungal species may contain different level of arabitol and manitol [*Bauer et al.*, 2008]. However, arabitol exhibited strong correlation with manitol (r = 0.98, p < 0.001) in this study, suggesting that they derived from similar sources (Fig. 6). Arabitol also showed significant correlation with inositol (r = 0.75, p < 0.001), indicating partly emitted from similar sources (Fig. 6]. Moreover, positive correlations were observed between nss-Ca^{2+} and arabitol (r = 0.40, p < 0.05) as well as manitol (r = 0.43, p < 0.05) during this study period (Fig. 6). It can be assumed that arabitol and manitol might be partly associated with soil dust (soil microbe) in the atmosphere. In contrast, erythritol showed similar temporal variation with levoglucosan (Fig. 5 & chapter 3; Fig. 3), indicating that erythritol might be released from biomass burning activities.

5.3.2. Seasonal variations

5.3.2.1. Seasonal variations of primary sugars

All primary sugars except xylose exhibited similar seasonal variations in summer/spring maxima and winter/autumn minima (Table 1, Fig. 7). Sucrose maximized in spring (ave. 160 ng m^{-3}), followed by summer (13.1 ng m^{-3}), autumn (1.46 ng m^{-3}), and winter (0.15 ng m^{-3}), respectively, which is comparable with previous study in Okinawa aerosols in Japan [*Zhu et al.*, 2015]. Fructose also showed similar seasonal trends with sucrose in spring maxima (ave. 7.77 ng m^{-3}), followed by summer (3.99 ng m^{-3}), autumn (0.81 ng m^{-3}), and winter (0.60 ng m^{-3}), consequently. The concentration plot of sucrose and fructose shows two sharply increased peaks during late spring (Fig. 3). It indicates that sucrose and fructose might be derived from similar sources.

In addition, correlation coefficient between sucrose and fructose (Fig. 4) also suggests their same sources. The similar seasonal trend was also observed for the deciduous forest, Japan due to the springtime pollen emission [*Miyazaki et al.*, 2012]. Higher standard deviation was observed for both of sucrose and fructose due to the large fluctuation in spring (Fig. 7). Sucrose is the predominant sugar in developing flower buds and is important in the phloem of plants [*Bieleski*, 1995]. *Graham et al.*, [2003] reported that fructose and sucrose can release together in daytime from pollen, fern spores and other "giant" bioaerosols. In spring, the air masses mainly come from the Oceanic region such as Arctic Ocean (48%), North Pacific Ocean (26%) and Bering Sea (26%) to Alaska (chapter 2, Fig. 3), where as very few sources of sucrose and trehalose are known to be present in Ocean. Based on above discussion, it can be predicted that during flowering or growing local vegetation/plants, largely contribute to sucrose as well as fructose in Alaska aerosol.

The seasonal distribution of glucose shows high concentration in summer (20.4 ng m^{-3}), followed by spring (12.0 ng m^{-3}), autumn (3.33 ng m^{-3}), and winter (2.62 ng m^{-3}), respectively. Similar seasonality was observed for trehalose in summer maxima (7.17 ng m^{-3}) and winter minima (0.11 ng m^{-3}) (Table 1). Significant correlation was found between glucose and trehalose (r = 0.81, p < 0.001) (Fig. 8), indicating common sources for these two compounds. Probably, trehalose mainly release from terrestrial microbe or together with glucose from plant materials. *Fu et al.*, [2010] also reported similar sources for glucose and trehalose from tropical India site. Cluster analyses of backward trajectories (chapter 2, Fig. 3) in summer suggest that air masses mainly originate from Oceanic region where source of glucose and trehalose is ignorable. This result indicates that glucose and trehalose may be originated from regional boreal forest during blooming period of trees.

In contrast, xylose exhibited different seasonal pattern from those of other primary sugars (Table 1 and Fig. 7). It was most dominant in winter (4.25 ng m^{-3}), followed by autumn (1.64 ng m^{-3}), summer (0.29 ng m^{-3}), and spring (0.20 ng m^{-3}), respectively, which is similar with the biomass burning tracer of levoglucosan (chapter 3; Fig. 7). Significant correlation was also observed between xylose and levoglucosan (r = 0.75, p < 0.001) (Fig. 9), assuming that xylose associated with biomass burning activities in Alaska aerosols. A similar seasonal trend has been proposed for xylose in the midwestern United States, with relatively lower abundances of 2.1 ng m^{-3} in winter, and has been attributed to biomass burning based on a good correlation with levoglucosan [*Sullivan et al.*, 2011].

5.3.2.2. Seasonal variations of sugar alcohols

Manitol was most abundant sugar alcohol, showing maximum in spring (44.3 ng m^{-3}), followed by summer (23.1 ng m^{-3}), autumn (2.86 ng m^{-3}), and winter (0.41 ng m^{-3}), respectively.

Arabitol also exhibited similar seasonal trend in spring maxima (34.9 ng m^{-3}) and winter minima (1.50 ng m^{-3}) (Table 1, Fig. 10). Arabitol and manitol are used to tracers for airborne fungal spore [*Lewis and Smith*, 1967; *Bauer et al.*, 2008] and they can also be emitted by the variety of microbes (e.g. bacteria), few algae's (e.g. green-algal lichens) [*Dahlman et al.*, 2003; *Matthias-Maser et al.*, 2000]. *Zhu et al.*, [2015] and *Yttri et al.*, [2007] also reported, arabitol and manitol as dominant sugar alcohols in Okinawa aerosols and various site of Norway, respectively. Their abundances were comparable throughout the year with strong positive linear correlation (r = 0.98, p < 0.001) (Fig. 6). Previous studies also observed such a relation implies common sources for arabitol and manitol [*Fu et al.*, 2012a; *Medeiros et al.*, 2006a].

Low level of inositol was observed in Alaska aerosols. Inositol was found most dominant in summer (0.61 ng m^{-3}), followed by spring (0.39 ng m^{-3}), autumn (0.13 ng m^{-3}), and winter (0.07 ng m^{-3}), consequently. Significant positive linear correlation between arabitol and inositol (r = 0.75, p < 0.001) (Fig. 6), suggesting that inositol originated from microbial activities. However, recent biological studies have proposed that inositol also acts as a functional component in regulating plant salt tolerance [*Golani et al.*, 2013], which conditions may favor for the production of inositol from plants. The meteorological factors such as relative humidity and temperature significantly affect the microbial (e.g., fungal, bacteria) activity [*Kim and Xiao*, 2005; *Malik and Singh*, 2004]. The microbial growth is enhanced in the atmosphere, in terms of the increasing relative humidity and temperature [*Sharma and Razak*, 2003]. The higher concentration of sugar alcohols during spring and summer, might be due to the high microbial activities.

In contrast, erythritol showed opposite seasonal pattern from those of other sugar alcoholos (Table 1 and Fig. 10). Erythritol was more abundant in winter (4.63 ng m^{-3}) and autumn (2.77 ng

m^{-3}) than in summer (1.02 ng m^{-3}) and spring (0.40 ng m^{-3}), that's behavior is similar with levoglucosan (chapter 3; Fig. 7). Significant correlation was also found between erythritol and levoglucosan (r = 0.66, p < 0.001) (Fig. 9), indicating that erythritol mainly associated with biomass burning activities in Alaska aerosols. *Fu et al.*, [2010] also reported similar source of erythritol and levoglucosan from biomass burning.

5.4. Summary

Primary sugars such as sucrose, glucose, fructose, trehalose, and xylose as well as four sugar alcohols such as arabitol, manitol, inositol, and erythritol were quantified in ambient aerosols from subarctic Alaska. All primary sugars except xylose showed higher concentrations in summer/spring and lower in winter/autumn, where as xylose was more abundant in winter/autumn than summer/spring. Sucrose was most dominant tracer among all the primary sugars throughout the study period. Sucrose maximized in spring (160 ng m^{-3}), followed by summer (13.1 ng m^{-3}), autumn (1.46 ng m^{-3}), and winter (0.15 ng m^{-3}), respectively. Fructose also exhibited similar seasonal behavior with sucrose might be owing to the developing flower buds. In contrast, glucose and trehalose showed similar seasonal trend with summer maximum and winter minimum, suggesting same source from plant materials. Moreover, similar seasonal pattern was observed between xylose and levoglucosan, suggesting originated from biomass burning.

All sugar alcohols except erythritol also showed similar seasonal variations with primary sugars in spring/summer maximum and winter/autumn minimum. Arabitol and manitol were more abundant in spring, followed by summer, autumn and winter. Positive linear correlation between nss-Ca^{2+} (tracer from soil dust) and arabitol/manitol indicates that arabitol and manitol

partly associated with soil dust. It can be hypothesized that arabitol and manitol which are known as microbial tracers might be derived from airborne fungal, terrestrial microbe as well as soil microbes. Positive correlation between inositol and arabitol suggest that they emit from same sources, whereas inositol was found more abundant in summer than spring and other seasons. Based on these results, it can also be predicted that during summer and spring time microbial activities were enhanced due to the higher temperature and relative humidity. In contrast, erythritol originated from biomass burning in this study, as it is showing similar seasonal trend with levoglucosan in winter maximum and spring minimum.

Cluster analysis of backward air masses trajectories to Alaska in all seasons indicate that air masses mainly originate from Oceanic region, where as 7 days backward trajectories can not reach the continent (chapter 2, Fig. 3). However, in winter and autumn time some air masses come with short distance from the regional area in Alaska, when the boreal forest and local vegetations are inactive for biogenic emission. In contrast, late spring and summer time are the growing season for Alaska boreal and tundra forest. During this blooming season, the vegetations are typically vary active, can release large amount of biogenic organic tracers in the atmosphere. Based on the results, it can be proposed that primary biological aerosol particles (PBAPs) tracers mainly derived from the regional boreal and tundra forest or local vegetations due to the high biological activities in spring and summer period.

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Table 1

Average concentrations of primary sugars and sugar alcohols (ng m^{-3}) measured in the Alaska aerosols.

| Species	summer			autumn			winter			spring		
	avg[a]	min	max	avg	min	max	avg	min	max	avg	min	max
primary sugars												
glucose	20.4	1.86	46.6	3.33	1.06	11.8	2.62	0.95	4.94	12.0	0.13	22.8
fructose	3.99	2.16	7.27	0.81	0.33	2.25	0.60	0.37	0.87	7.77	0.06	14.7
sucrose	13.1	3.09	69.2	1.46	0.14	7.28	0.15	0.10	0.32	160	0.02	364
trehalose	7.17	1.60	13.2	1.41	0.04	8.01	0.11	0.05	0.20	5.35	0.03	13.3
xylose	0.29	0.06	0.69	1.64	0.22	4.72	4.25	1.04	7.48	0.20	0.03	0.34
subtotal	44.9	8.77	137	8.65	1.79	34.1	7.73	2.51	13.8	185	0.27	415
sugar alcohols												
arabitol	22.0	9.75	36.2	5.65	0.54	24.1	1.50	0.62	2.92	34.9	0.09	89.7
manitol	23.1	7.35	41.5	2.86	0.24	14.2	0.41	0.11	1.10	44.3	0.06	116
inositol	0.61	0.19	1.41	0.13	0.08	0.32	0.07	0.03	0.11	0.39	0.01	0.92
erythritol	1.02	0.25	2.02	2.77	0.61	6.67	4.63	1.33	11.9	0.40	0.10	0.65
subtotal	46.7	17.5	81.1	11.4	1.47	45.3	6.61	2.09	16.0	80.0	0.26	207
Total PBAP tracers	91.2	26.3	218	20.1	3.26	79.4	14.3	4.60	29.8	265	0.53	622

[a]avg :average.
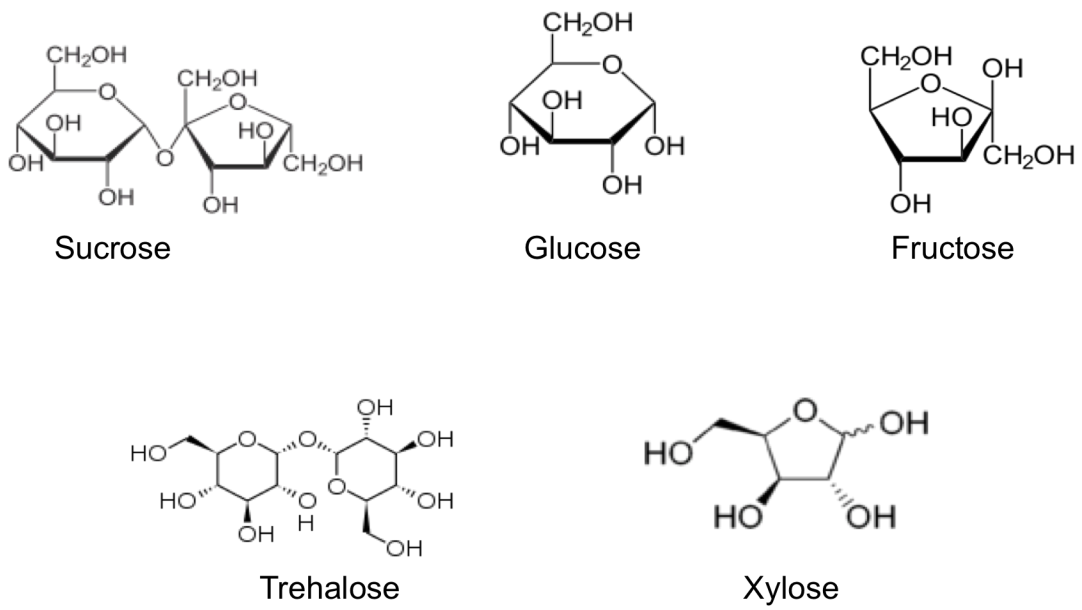
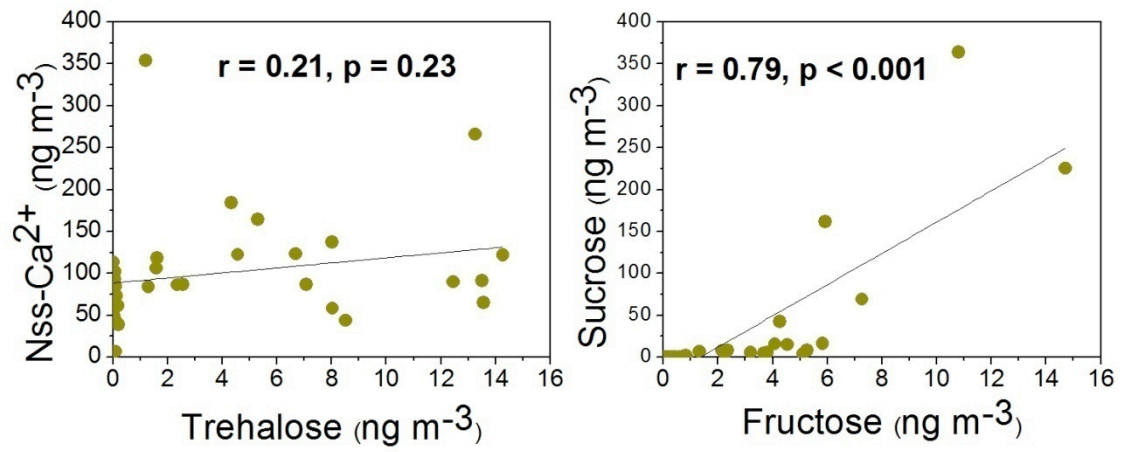**Fig. 1**. Chemical structures of primary sugar compounds.
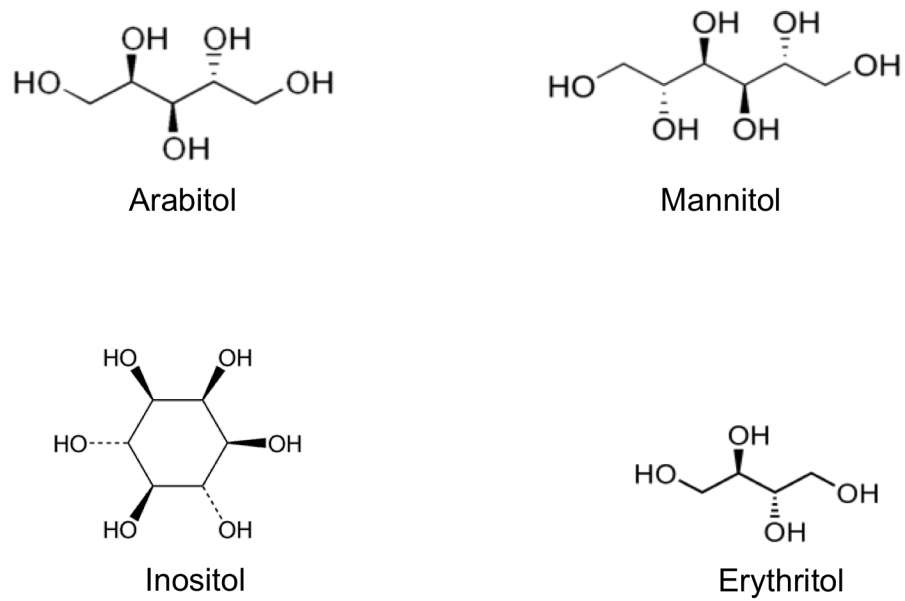
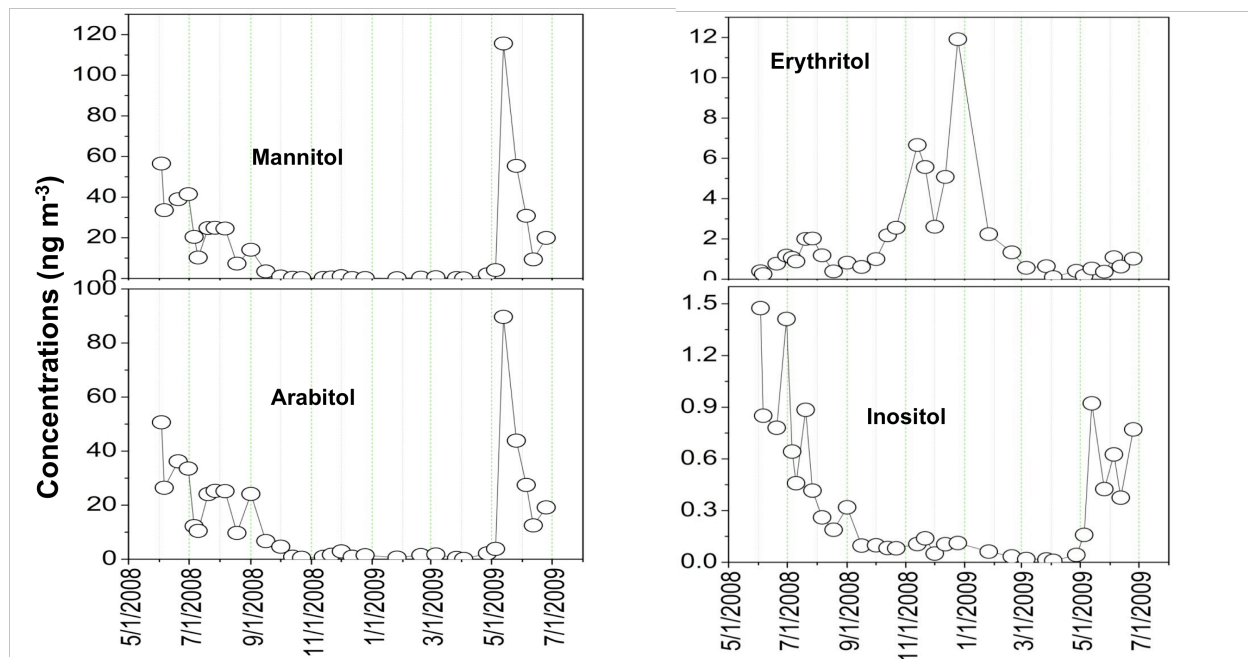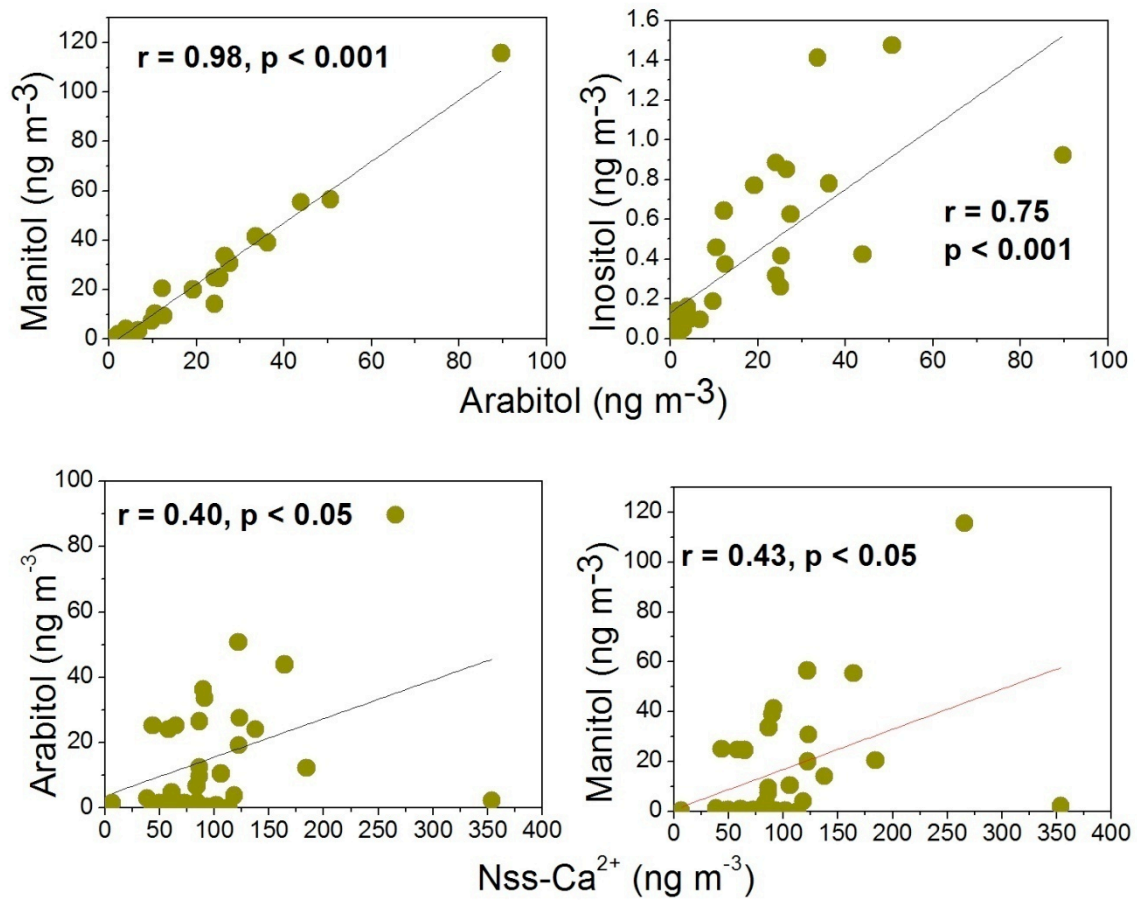**Fig. 2**. Chemical structures of sugar alcohol compounds.
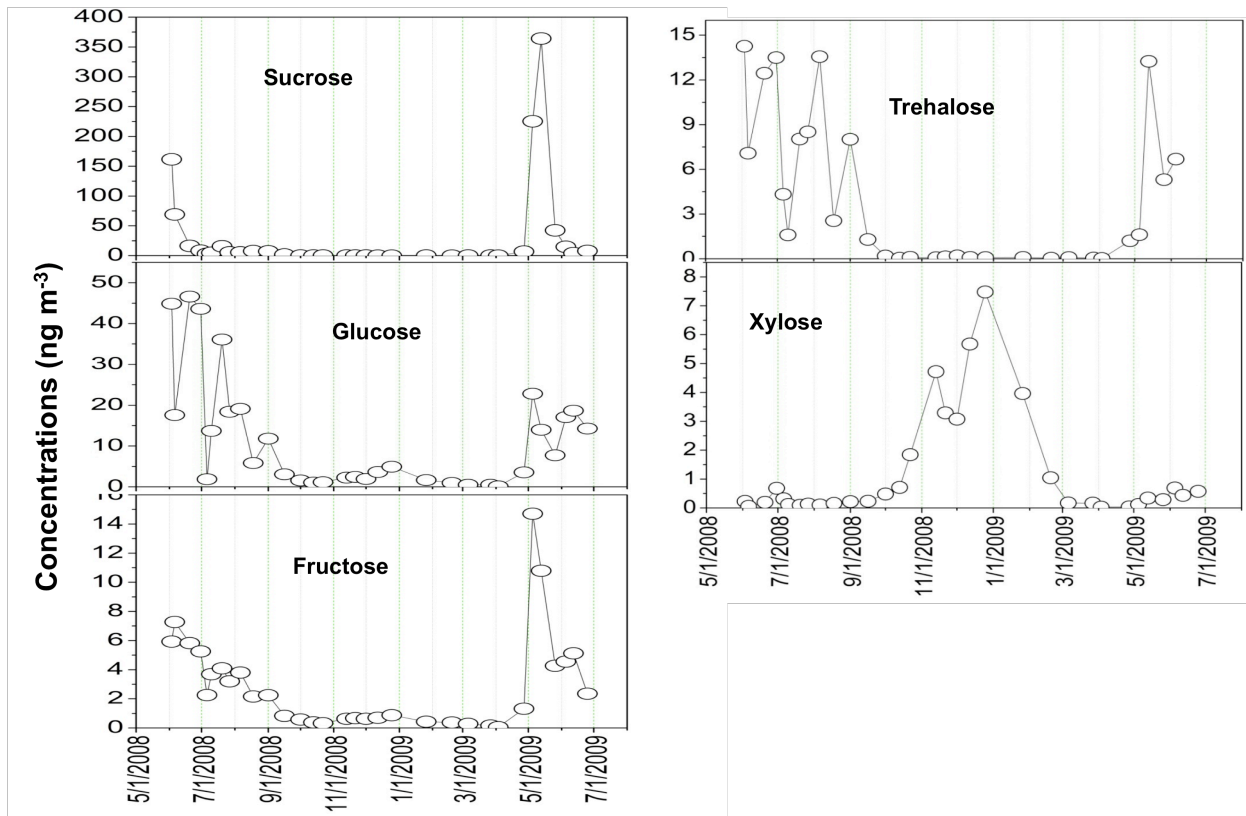
Fig. 3. Temporal variations of primary sugars in Alaska aerosols.

Fig. 4. Correlations among fructose, sucrose, trehalose and nss-Ca^{2+}.

Fig. 5. Temporal variations of sugar alcohols in Alaska aerosols.

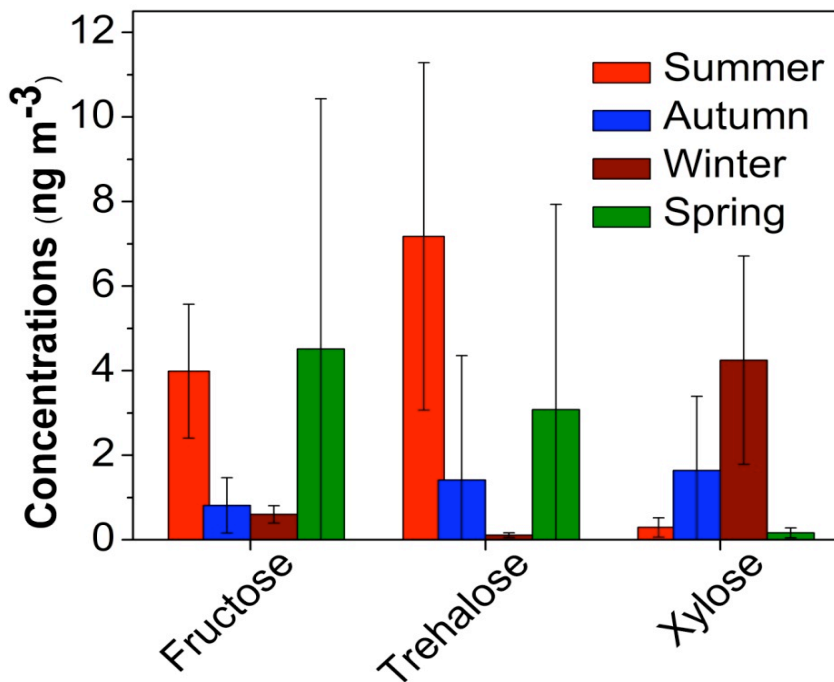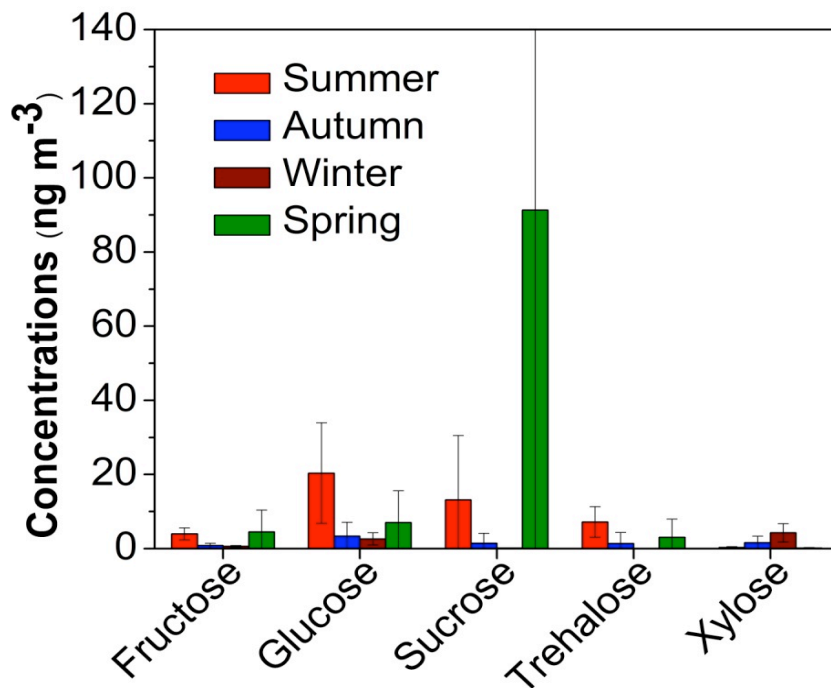**Fig. 6**. Correlations among arabitol, manitol, inositol, and nss-Ca^{2+} in Alaska aerosols.

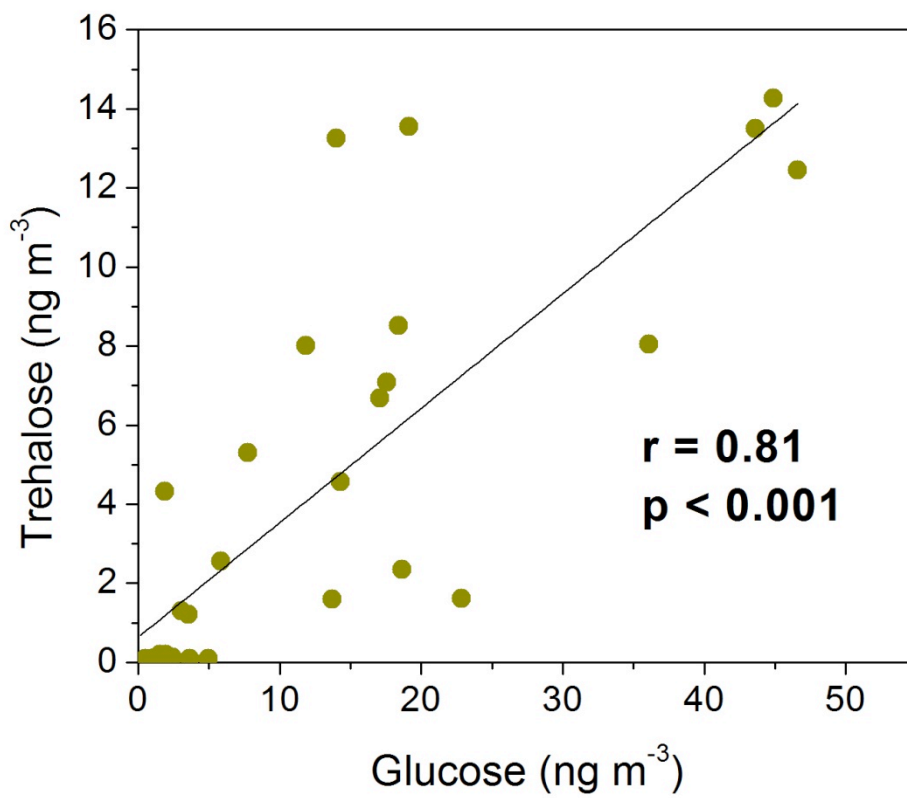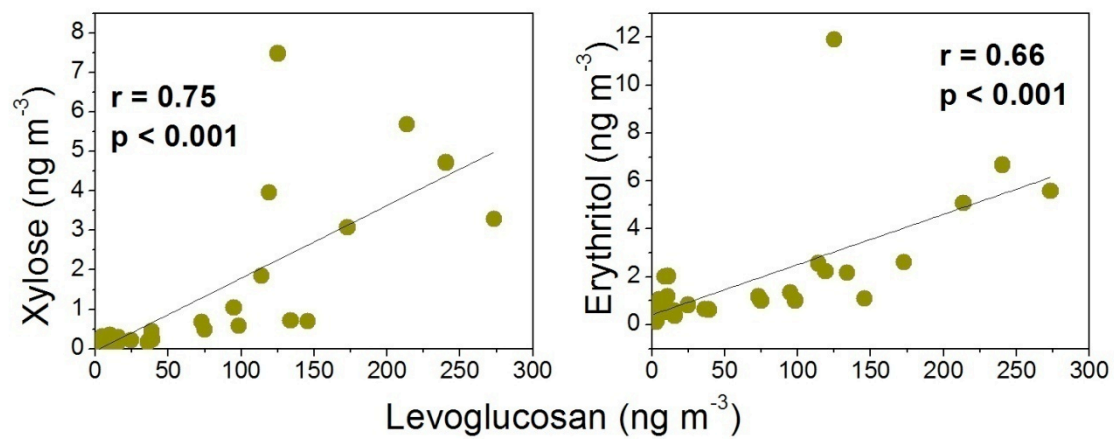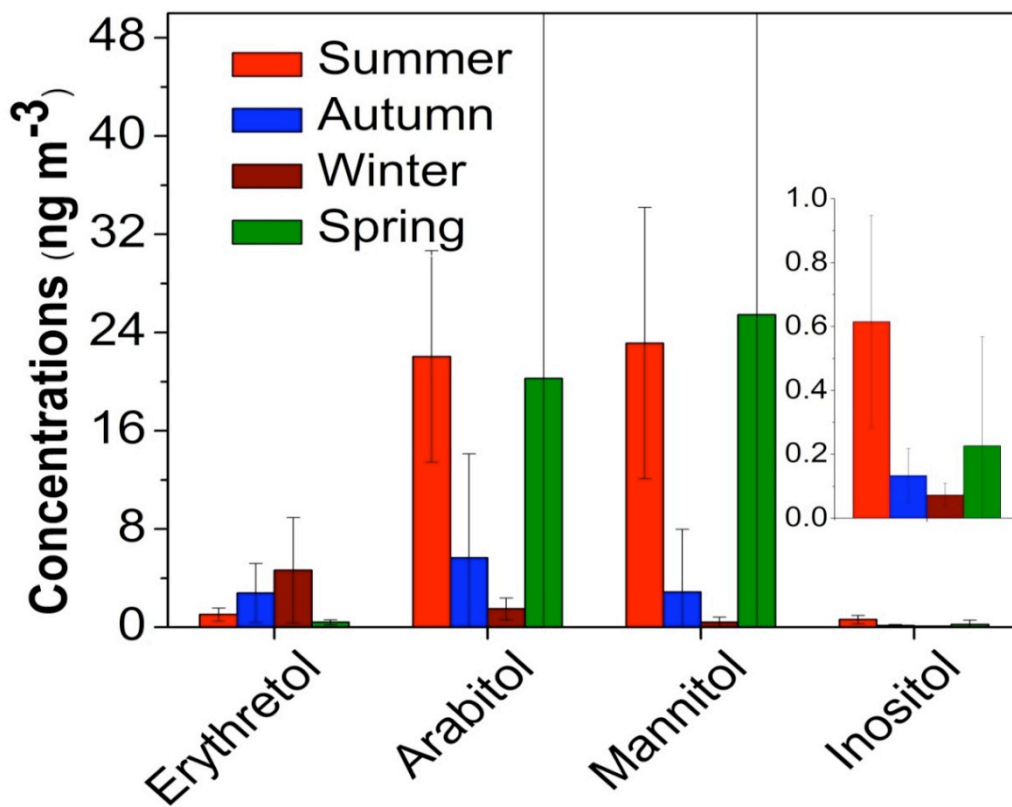**Fig. 7**. Seasonal variations of primary sugars in Alaska aerosols

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Fig. 8. Correlations between glucose and trehalose in Alaska ambient aerosols.

Fig. 9. Correlations among levoglucosan, xylose and erythritol.

Fig. 10. Seasonal variations of sugar alcohols in Alaska aerosols.

Chapter 6: Source apportionment of organic compounds

6.1. Positive Matrix Factorization (PMF) Analysis

Positive matrix factorization (PMF) is a statistical source apportionment model which is developed by U. S. Environmental Protection Agency (EPA PMF version 5.0). It is a multivariate factor analysis tool that decomposes a matrix X (n x m) of chemically speciated samples into two matrices including source contributions (G, n x p) and source profiles (F, p x m) [*Paatero and Tapper*, 1994] for the number of samples (n), the number of chemical species (m), and the number of factors (p) (*US EPA*, 2014]. PMF confirm that all of the species profiles (matrix F) are non-negative, each sample has a non-negative source contribution (matrix G), and the sum of the speculated elemental mass contributions for each source must be less than or equal to the total measured mass for each element. The mass balance eqn (1) in the PMF model is written in the following way:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (1)$$

where x_{ij} is the concentration of jth chemical species in the i number of samples, g_{ik} is the mass concentration in the ith sample from the kth source, f_{kj} is the fraction of chemical species j from the source of k, and e_{ij} is the residual of species j in the ith sample.

PMF accept the adjustment of each data point based on the uncertainty measurements. In this process, the influence of data points with lower or more uncertain concentrations can be minimized. The PMF uncertainty function is given (eqn 2) -

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \qquad (2)$$

where u_{ij} is the user assigned uncertainty in the jth species for the ith sample. The PMF model solves for the Q minima using the input provided by the user to the program [US EPA, 2014].

PMF is a powerful statistical tool that can resolve potential sources contributing to ambient particle levels which has been widely used with elemental data and to a more limited extent, on organic molecular markers [*Jaeckels et al.*, 2007]. The model analyzes sets of ambient aerosol data to estimate the number of sources of particulates matter, the chemical composition of each source, and the value that each source contributes to each sample, based on the compositional data of aerosols and major representative markers for difference sources. A recent study applied PMF modeling, where organic molecular markers was used based on apportioning ambient PM to motor vehicle emission, secondary organic aerosol, wood combustion, and two point sources [*Jaeckels et al.*, 2007].

6.2. Method

In this study, data were processed in the PMF model recommended by *Polissar et al.* [1998]. Based on the replicate analyses, 15% of the uncertainty for the measurement of organic compounds was applied to PMF analysis. The method detection limits (MDLs) of organic compound were assigned using the analytical values of 0.0015–0.0081 ng m^{-3}. When the measured concentrations fell below the MDL, 1/3 of MDL was assigned to the data points and the corresponding uncertainties were 5/6 of MDL. The signal to noise ratios of different input chemical species ranged from 5.7 to 19.0. Based on given understanding of organic components sources, 3–7 factors were tested and 4 interpretable factors were determined. The minimal robust and true Q values of the base run were 1798 and 1776, respectively.

6.3. Results and Discussion

6.3.1. Source identification and factor profiles

The detected anhydro-sugars, lignin and resin acids, biogenic SOA tracers, primary sugars and sugar alcohols were subjected to positive matrix factorization (PMF) analysis to constrain their source classifications using PMF model. Organic carbon (OC), elemental carbon (EC) some inorganic ions also used to investigate possible different sources. During model convergence, OC was used as the sum of total variables. Fig. 1 shows composition profiles for the four factors resolved by PMF.

Factor 1 is dominated by primary sugars, sugar alcohols and biogenic SOA tracers which should be originated from vegetation. Factor 1 includes 2-methyltetrols (81%), C5 alkenes (81%), 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (57%), trehalose (65%), manitol (57%), sucrose (56%), and glucose (54%) (Fig. 1), which are considered as tracers from biogenic emission. Factor 2 is characterized by levoglucosan (82%), xylose (87%), erythritol (86%), vanillic acid (92%), dehydroabietic acid (89%), β-caryophyllinic acid (70%), and NO_3^- (91%), suggesting that the components associated with biomass burning. Factor 3 was abundantly loaded by arabitol (48%), manitol (35%), fructose (41%), and MSA (48%), indicating that the chemical species are derived from the microbial activities. It should be noted that arabitol, manitol and fructose also showed loadings in Factor 2, suggesting vegetation can contribute in part to these sugar compounds. Factor 4 is dominated by inorganic ions, probably originated from soil dust and some anthropogenic activities.

6.3.2. Source contributions

PMF results can be further utilized to calculate the relative source contributions to the amount of ambient organic carbon using a multiple linear regression between the isolated factor strengths and measured organic carbon [*Song et al.*, 2001]. Results of this analysis are presented in Fig. 2. Biomass burning was most abundant source (49.2%), followed by biogenic vegetation (22.5%), biogenic microbial (14.4%), and anthropogenic with soil dust (13.9%) sources, respectively during this study period. This result is consistent with annual average observation values of identified organic components, where as anhydro-sugars were most dominant (50.8%), followed by primary sugars (16.9%), sugar alcohols (14.5%), biogenic SOA tracers (12.8%), and lignin & resin products (5.0%), respectively (Fig. 3). These results indicate that biomass burning was more important source compare to biogenic emissions in Alaska atmosphere during the study period.

6.4. Summary

Positive matrix factorization (PMF) modeling was applied to identify source classifications and relative source contributions for identified organic components such as anhydro-sugars, lignin and resin acids, biogenic SOA tracers, primary sugars and sugar alcohols. In this regard, four interpretable factors were detected for different sources. The results of PMF analysis suggest that the contribution of biomass burning to Alaska atmosphere was most abundant than biogenic vegetation and microbial activities. The air mass backward trajectories from June 2008-June 2009 indicates that air masses mainly originated over Oceanic region and partly with short distance from regional area and traveled to Fairbanks, Alaska (chapter 2, Fig 2, 3). Based on these results, it can be concluded that the quantified organic components mainly emitted from

regional sources such forest fire, domestic burning, boreal and tundra forests, etc. Air mass forward trajectories (chapter 2, Fig. 4) suggest that the Alaska air masses can be transported to Arctic, resulting Alaska pollutants might be influenced the climate of Arctic region.

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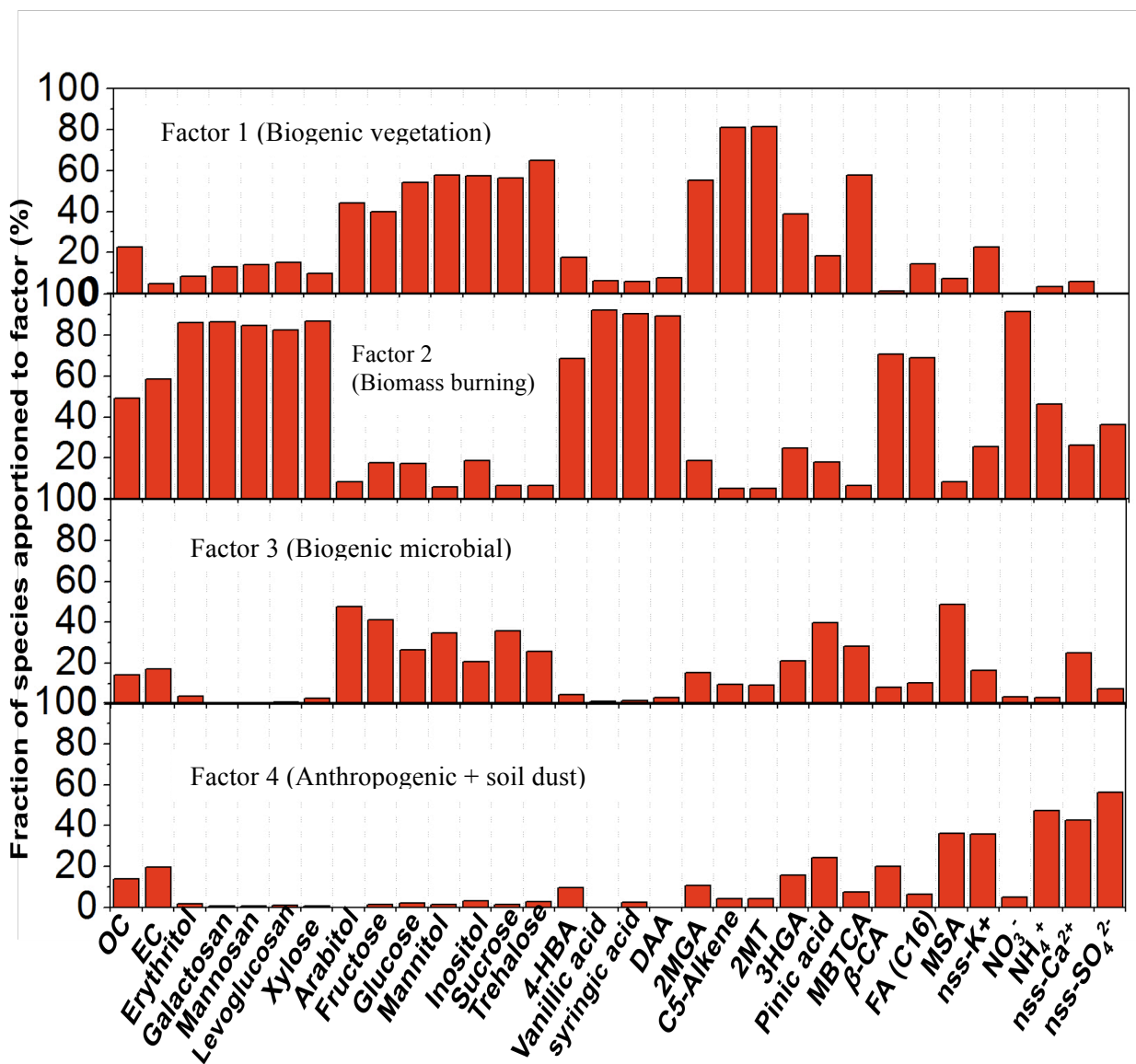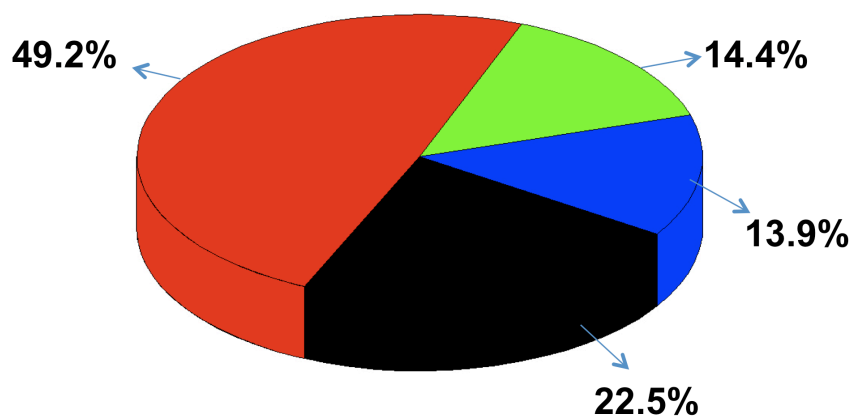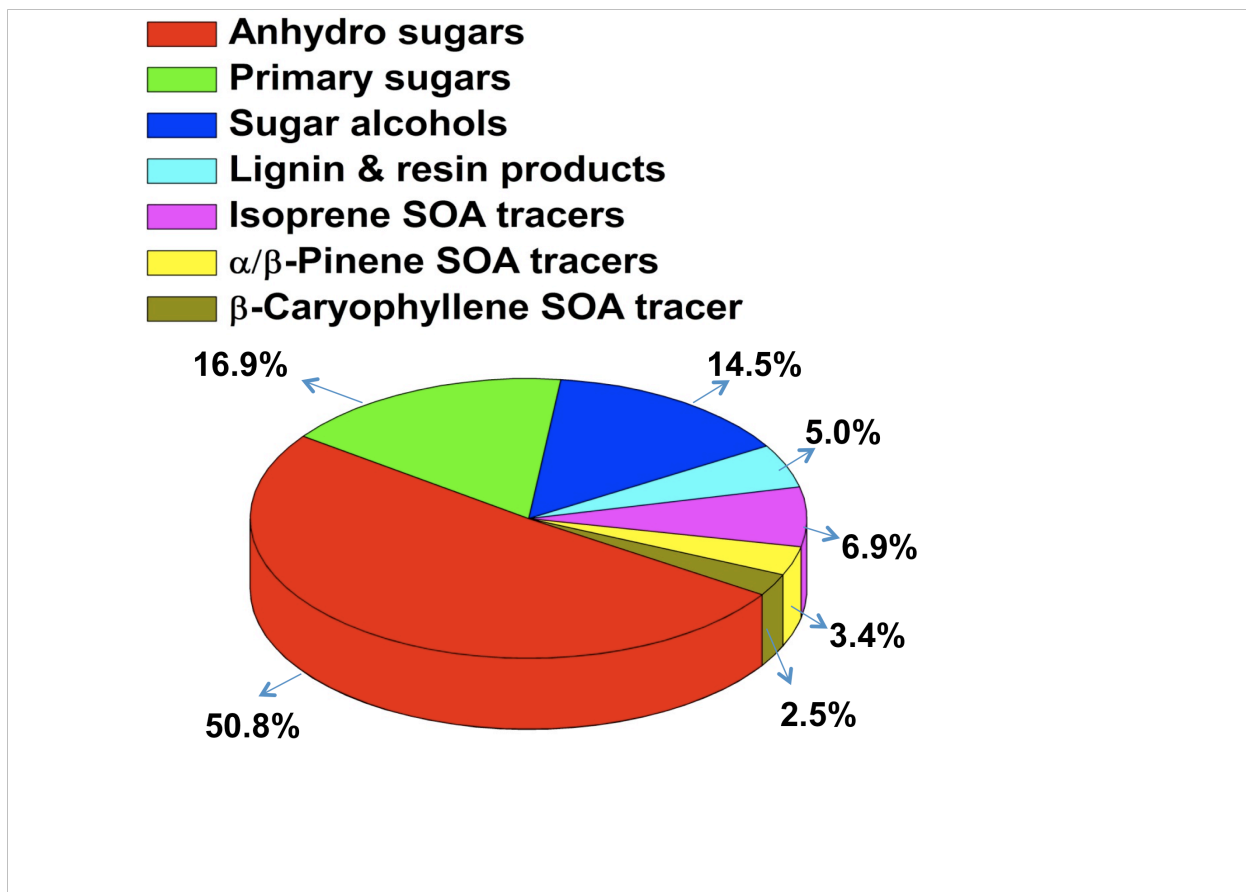
U.S. EPA, EPA-PMF 5.0, 2014.

Fig. 1. Composition profiles (% of total each species) for the four factors resolved by PMF analysis based on identified chemical components.

Fig. 2. Relative source contribution of identified chemical species to organic carbon (OC).

Fig. 3. Annual compositions based on concentration to total quantified organic compounds.

Chapter 7. Summary and Conclusions

In this study, the molecular compositions and seasonal variations of anhydro-sugars (levoglucosan, galactosan and mannosan), lignin & resin acids (4-hydroxybenzoic, syringic, vanillic and dehydroabietic acids), biogenic SOA tracers (isoprene, α-/β-pinene and β-caryophyllene SOA tracers), primary sugars (sucrose, glucose, fructose, trehalose, and xylose), and sugar alcohols (arabitol, manitol, inositol, and erythritol) were observed in the ambient aerosols from the central Alaska, USA. Anhydro-sugars and lignin & resin acids are considered as specific tracers from biomass burning emissions, where as they are produced by the combustion of wood/vegetation, containing cellulose, hemicelluloses, lignin and resin. Levoglucosan was as a dominant biomass burning tracers with a concentration range of 1.07-273 ng m^{-3} (average 66.8 ng m^{-3}) followed by its two isomers: mannosan (0.22-63.1 ng m^{-3}; ave. 15.0 ng m^{-3}) and galactosan (0.12–39.4 ng m^{-3}; ave. 9.88 ng m^{-3}). Galactosan and mannosan exhibited similar temporal and seasonal trends with levoglucosan. Levoglucosan showed clear seasonal variability with winter maximum (ave.145 ng m^{-3}) and spring minimum (12.3 ng m^{-3}). Similar temporal and seasonal variations with levoglucosan were also observed for all lignin and resin acids. Dehydroabietic acid, one of the most dominant compounds for lignin and resin products, showing high level in winter (20.7 ng m^{-3}) and low level in spring (0.62 ng m^{-3}). The values of L/M ratios (2.30 to 7.84) indicate that biomass burning tracers in the Alaska atmosphere mainly originated from soft wood burning.

Significant correlations of levoglucosan with EC (r = 0.67, p < 0.001), OC (r = 0.51, p < 0.001), and WSOC (r = 0.61, p < 0.001) demonstrated that biomass burning is an important source for carbonaceous components in Alaska aerosols. Levoglucosan contributed 2.92% to WSOC and 1.62% to OC with high level in winter (WSOC; 6.26% and OC; 3.63%) indicate that

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contribution of biomass burning to Alaskan aerosols is more important in winter period. Wildfire or forest fire has been considered as a major source of biomass burning tracers in the Alaska region. However, the analyses of air mass back trajectories and fire spots demonstrated that indoor burning activities such as residential heating is more significant source for biomass burning tracers. These results provide important information to better understand the effect of biomass burning on subarctic atmosphere.

Biogenic SOA tracers are the photo-oxidation products of BVOCs such as isoprene (2-methylglyceric acid, C_5-alkene triols and 2-methyltetrols), α-/β-pinene (pinonic acid, pinic acid, 3-hydroxyglutaric acid and MBTCA) and β-caryophyllene (β-caryophyllinic acid). Isoprene oxidation products exhibited much higher concentrations in summer (ave. 8.77 ng m^{-3}), whereas α-/β-pinene and β-caryophyllene oxidation products showed the highest values in spring (3.55 ng m^{-3}) and winter (4.04 ng m^{-3}), respectively. Higher contributions of isoprene- and α-/β-pinene-SOA tracers to SOA formation in summer and spring may be due to the larger emissions in blooming season and relatively high levels of oxidants (e.g., OH). The estimation of isoprene-derived SOC using tracer based method, is about 5 times higher than α-/β-pinene-derived SOC and 2 times higher than β-caryophyllene-SOC. Based on air mass back trajectory, it can be proposed that boreal black spruce forest and tundra could be the major sources of isoprene and α-/β-pinene-SOA. In contrast, β-caryophyllene- SOA tracer might be emitted from biomass burning due to high concentration in winter and positive correlation with levoglucosan (r = 0.65, p < 0.001). Based on SOA tracers in this study, it should be hypothesized that isoprene is an important contributor for biogenic SOA than α-/β-pinene and β-caryophyllene in subarctic Alaska, but emphasizes that sesquiterpene derived from residential biomass burning largely contributes.

In this study, all primary sugars and sugar alcohols except xylose and erythritol were more abundant in spring/summer compare to winter/autumn, where as xylose and erythritol showed higher concentration in winter/autumn than spring/summer. Sucrose was most dominant tracer (30.5 ng m^{-3}) among all the primary sugars and sugar alcohols, maximized in spring (160 ng m^{-3}), followed by summer (13.1 ng m^{-3}), autumn (1.46 ng m^{-3}), and winter (0.15 ng m^{-3}), respectively. Fructose also showed similar seasonal trend with sucrose might be owing to the developing flower buds. However, glucose and trehalose exhibited similar seasonal variation with summer maximum and winter minimum, suggesting similar source from plant materials. Moreover, high levels of arabitol and manitol were observed in spring, followed by summer, autumn and winter, consequently. Similar seasonal trend with sucrose/fructose and positive correlation with nss-Ca^{2+} of arabitol/manitol, indicating that sugar alcohols might be derived from airborne fungal, terrestrial microbe and also soil microbes. Based on these results, it can be hypothesized that microbial activities could be enhanced during spring and summer in Alaska atmosphere due to the higher temperature and relative humidity. In contrast, xylose and erythritol originated from biomass burning due to their similar seasonal behavior with biomass burning tracer of levoglucosan. Based on above discussion and backward air masses trajectories, it can be proposed that primary biological aerosol particles (PBAPs) tracers mainly originated from Alaskan regional boreal and tundra forest or local vegetations due to the high biological activities during spring and summer period.

The present study demonstrates that biomass burning tracers are dominant in winter and autumn, whereas primary sugars, sugar alcohols and biogenic SOA tracers are more abundant in summer and spring. Based on measured organic tracers in this study, biomass burning tracers (107 ng m^{-3}) were observed more abundant followed by primary sugars (50.8 ng m^{-3}), sugar

alcohols (34.9 ng m^{-3}), and biogenic SOA tracers (27.1 ng m^{-3}), respectively throughout the study period. Positive matrix factorization analysis (PMF) also suggest that the contribution of biomass burning (49.2%) was most dominant than biogenic-vegetation (22.5%) and biogenic-microbial (14.4%). These results indicate that biomass burning is a potential source in Alaska aerosols. Significant amounts of primary biological aerosol particles (PBAPs) suggest that there is some impact of bio-aerosols on the atmosphere over interior Alaska. I observed short distance backward air mass trajectories and mixed air masses in all seasons which are mainly originate over Ocean, suggesting that regional emission is more important source for organic aerosols in Alaska atmosphere. The analysis of forward trajectories indicates that Alaska pollutants can be transported to the Arctic, which might be influenced the Arctic climate. The current study presents for the first time one-year observation on organic tracers in the subarctic region. Thus, the study will provide useful information about the effect of organic aerosols on Arctic or subarctic atmosphere and it will also be helpful for further long term climate studies in this region.