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acids, pyruvic acid, α -dicarbonyls and fatty acids from southern
Alaska since 1665AD: A link to climate change in the Northern
Hemisphere**

By

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The work of this Ph. D. thesis belongs to all human beings!

Abstract

Alaskan ice core (180 m long, 343 years) has been analyzed for a homologous series of normal ($C_2 - C_{11}$), branched chain ($iC_4 - iC_6$), unsaturated (maleic, fumaric, methylmaleic and phthalic), multifunctional dicarboxylic (malic, oxomalonic and 4-oxopimelic), ω -oxocarboxylic acids ($\omega C_2 - \omega C_9$), pyruvic acid, glyoxal and methylglyoxal using gas chromatography (GC/FID) and GC/mass spectrometry (GC/MS) to understand historical changes in water soluble organic aerosols. Similarly, homologous series of straight chain fatty acids ($C_{12:0} - C_{30:0}$) has been detected by using GC/FID and GC/MS system.

Predominance of oxalic acid was found followed by adipic and succinic acid. Molecular distributions of ω -oxocarboxylic acids are characterized by the predominance of 9-oxononanoic, followed by 4-oxobutanoic and glyoxylic acids. Historical concentrations of diacids, oxoacids and α -dicarbonyls are formed by the oxidation of precursor compounds emitted from biogenic and biomass burning activities and which are controlled under climate oscillations and similar meteorological parameters. Historical trends of monoterpene and isoprene SOA tracers showed significant concentrations since the 1660s, which are associated with ambient atmospheric temperature and controlled by Aleutine Low.

Molecular distributions of fatty acids are characterized by even carbon number predominance with a peak at palmitic ($C_{16:0}$) followed by oleic ($C_{18:1}$) and myristic acid ($C_{14:0}$). The historical trends of short-chain fatty acids, together with correlation analysis with inorganic ions and organic tracers suggest that short-chain fatty acids (except for $C_{12:0}$ and $C_{15:0}$) were mainly derived from sea surface micro layers. In contrast, long-chain fatty acids ($C_{20:0} - C_{30:0}$) are originated from terrestrial higher plants, soil organic matter and dusts, which are also linked with Greenland Temperature Anomaly (GTA). Hence, this study suggests that Alaskan fatty acids are strongly influenced by Pacific Decadal Oscillation/North Pacific Gyre Oscillation and/or extra tropical North Pacific surface climate and Arctic Oscillation.

Organic tracers in ice core were derivatized with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride (TMCS) and pyridine and the derivatives were analyzed using GC/MS system. Levoglucosan, dehydroabietic and vanillic acid showed higher concentration with many sporadic peaks since 1660s-1830s, 1913, and 2005. Moreover, there are a few discrepancies of

higher spikes among them after 1980s with sporadic peaks in 1994-2007 for dehydroabietic acid. Historical trends of levoglucosan, dehydroabietic and vanillic acid showed that biomass burning activities from resin and lignin phenols from boreal conifer trees and other higher plants and grasses were significant before 1840s and after 1980s in the source regions of southern Alaska.

Nitrite (NO_2^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and methanesulfonate (CH_3SO_3^-) were determined for an ice core of the Aurora Peak in southeast Alaska using ion chromatograph. They have common periods for higher spike during the years 1665-2008. They are attributed to the same source regions and similar pathways. Interestingly, we found multi-decadal scale atmospheric transport from lower to higher latitudes in the North Pacific, which is reflected in historical concentration trends of anions. Moreover, correlation of levoglucosan with NH_4^+ , NO_3^- , SO_4^{2-} and NO_2^- suggests that these anions and cations are poor tracer of biomass burning activities in the source regions of southern Alaska. Hence, this study reveals a new dimension of anions periodic cycles in the North Pacific region, which may alter the concept of other ice core studies in the Northern and Southern Hemisphere.

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Chapter 1: Introduction

1.1 Ice Core Study

The sun and all the parts of the Earth, e.g., the oceans, atmosphere, landmasses, snow-ice masses, all life, and inner earth, are some factors of the paleoclimate. Researchers have established the existence of a climate change on Earth that is characterized by complex integration and feedback. Changes in any one part of the system affect all the others and ultimately result in climate change (e.g., geochemical cycle). Climate change is a continuous process. This much we have learned about the climate system; but beyond this we are less knowledgeable. How do the parts of the system interact? How will specific changes in one part affect the others and, ultimately, the climate? What patterns of processes occur to produce the changes we have observed in this study such as multi-decadal variations of low molecular weight diacids, biomass burning tracers and other organic and inorganic species for an ice core of the saddle of Aurora Peak from southern Alaska?

Long cylinders of glacial ice have been recovered by drilling over glaciers and/or ice sheet in southern Alaskan region (e.g., saddle of the Aurora Peak), Greenland (e.g., GRIP, GISP2, 20D and Site-J), Antarctica (e.g., Vostok, Dome A and Dome C), and high mountains (e.g., Mt. Everest and Tibetan ice core) around the world. Scientists retrieve these cores to look for records of climate change over the last few decades to 800 kyr (800,000 years) for the EPICA ice core (*Augustin et al., 2004*). The time resolution (i.e., the shortest time period which can be accurately distinguished) depends on the amount of annual snowfall, and reduces with depth as the ice compacts under the weight of layers accumulating on top of it. Upper layers of ice in a core correspond to a single year or sometimes a single season.

Ice cores studies were begun in the 1960s to complement other climate studies based on deep-sea cores, lake sediments, and tree-ring studies (*Dansgaard, 1964; Dansgaard et al., 1969; references therein*). Since then they have revealed previously unknown details

of atmospheric geochemical cycles (i.e., chemical and physical composition), temperature, and abrupt changes in climate. In other words, these include proxies for temperature, ocean volume, precipitation, gas composition of the lower atmosphere, production, degradation and atmospheric transport of chemical compounds (e.g., isomers and photochemical oxidations), volcanic eruptions, solar variability, sea-surface productivity, desert extent, and forest fires activities. Such changes include flicker that appear to occur in periods lasting only 3 to 10 years much more quickly than the traditional view of the pace of climate shifts.

Abrupt changes (e.g., Great Climate Shift in the Northern Hemisphere and abrupt change of organic compounds after the 1850s in the saddle of Aurora Peak) are of great concern for those who model future changes in climate and their potential impacts on society.

There are many long term and short-term ice core records and their chemical compositions have been documented from the Southern and Northern Hemisphere (SH/NH). As snow and ice accumulates on polar and alpine ice caps and ice sheets as a response to monthly, seasonal, annual, decadal and multi decadal climate change through time, it lays down a record of the environmental conditions at the time of its formation, ablation and accumulation. Seasonal effect is very important to alter the chemical compositions of ice sheet as well as glayers. For instance, near the glacier surface the winter layer is normally light in colour, while summer layer is darker due to partial melting and changes of chemical composition and dust impurities (*Nesje and Dahl 2000*). Analyses of ice cores from high altitude and high latitudes, where little or no surface melting takes place during the ablation season, have demonstrated that these contain a great deal of paleo-environmental information (i.e., decadal to penta-decadal climate oscillation, e.g., Pacific Decadal Oscillation, Arctic Oscillation and Greenland Temperature Anomaly). Moreover, aerosol (biogenic and anthropogenic emission) and dust particles can give information about the history of long and short range atmospheric transport which are

associated with geochemical cycles in the NH and SH.

For instance, NO_3^- is independent to the snow accumulation rate for an ice core records of the Dome C and other studies of Antarctica due to long range atmospheric transport, which can reveals many paleo-environmental information at a times for the SH [Legrand and Kirchner, 1990; Legrand and Delmas, 1986, 1988]. Similarly, organic compounds of the Greenland ice core [Kawamura *et al.*, 1999] has good agreement with reconstructed Arctic temperature departures [Jacoby and D'Arrigo, 1989], which can be correlated with multi-decadal climate oscillations in the NH. Moreover, this study also indicates the decadal variations of organic and inorganic compounds, which can reveals the new dimensions of geochemical cycle in the North Pacific regions (Pokhrel *et al.*, 2014). Hence, these results clearly showed that larges in the paleoclimate are imprinted as a organic and inorganic species in the SH and NH, which are associated with the Earth system.

1.2. Importance of Paleoclimate

Deep ice core records, e.g., from Lake Vostok, Antarctica, the Greenland Ice Sheet Project, North Greenland Ice Sheet Project and EPICA (eight glacial cycles), similarly shallow ice core from Russian, Canadian and Alaskan glaciers and other many parts of the world (Augustin, *et al.*, 2004; Sato *et al.*, 2014; Legrand and Mayewski, 1997, *references therein*) were analyzed for trapped gases (e.g., organic and inorganic species), stable isotope ratios and pollen trapped within the layers to better understand the paleoclimate. Paleoclimate is the study of changes in climate through time, ranging from studies of the last century to millions of years. There are many reasons for climate changes through time, including changes in chemical compositions of the atmosphere or dust/soot in the atmosphere (Kawamura *et al.*, 2001; Kaspari *et al.*, 2007, 2009a, 2009b). The reason, why we are interested in Earth's climate in the past, is that it helps us to better understand how different parts of the climate (ocean, atmosphere, clouds,

vegetations, glaciers, etc.) interact with one another and how climate might change in the future in response to man-made changes. There are two main ways to study paleoclimate: by measuring changes in climate through time and by running computer models. Climate changes can be measured by looking at the chemical or physical properties of materials formed at different times, such as old trees, fossils, ice and air bubbles in glaciers, and sediments at the bottom of lakes and oceans (*Meehl et al., 2013; Seki et al., 2011,2012, Barclay et al., 1999; Legrand and Mayewski, 1997; Kawamura et al., 1996; Osada and Langway, 1993*).

Hence, paleoclimate is important for past, contemporary, and future issues. Understanding past climate helps us to explain how current ecosystems came to be. For instance, climate typically controls types of vegetation growing in a particular area. Furthermore, paleoclimate provides data that we can use to model and predict both current and future climate change scenarios.

1.3. Atmospheric Aerosol for an Ice Core

An aerosol is defined as a colloidal system of solid or liquid particles in a gas. In other words, aerosols are the systems consisting of very small, invisible for the naked human eye and liquid or firm particles that remain suspended in gas or in air. Atmospheric aerosols have significant local, regional and global impacts (*e.g., Ramanathan et al., 2001*). Local impacts include vehicular emissions, wood burning fires and industrial processes that can lead to urban air pollution (*Kawamura et al., 2004, references therein*) and possible adverse health effects (*Pope et al., 2002, references therein*). Regionally, aerosols can be transported from areas of high emissions to relatively clean remote regions. Aerosols have the potential to significantly influence our entire planet through their role in heterogeneous chemistry in the troposphere and stratosphere. They scatter and absorb visible radiation, limiting visibility (*Ramanathan et al., 2001*). They affect the Earth's climate both directly (by scattering and absorbing radiation) and

indirectly (by serving as nuclei for cloud formation). They provide sites for surface chemistry and condensed-phase chemistry to take place in the atmosphere (*Kawamura et al, 1996b; Kawamura and Gagosian, 1987*).

Atmospheric aerosols originate from the condensation of gases and from the action of the wind on the Earth's surface. Fine aerosol particles (less than 1 μm in radius) originate almost exclusively from condensation of precursor gases. For instance, sulfuric acid (H_2SO_4) is produced in the atmosphere by the oxidation of sulfur dioxide (SO_2) emitted from fossil fuel combustion, volcanoes, and other sources. Mechanical action of the wind on the Earth's surface emits sea salt, soil dust, and vegetation debris into the atmosphere. These aerosols consist mainly of coarse particles 1-10 μm in radius. Particles finer than 1 μm are difficult to generate mechanically because they have large area-to-volume ratios and hence their surface tension per unit aerosol volume is high. Particles coarser than 10 μm are not easily lifted by the wind and have short atmospheric lifetimes because of their large sedimentation velocities (e.g., Figure 1).

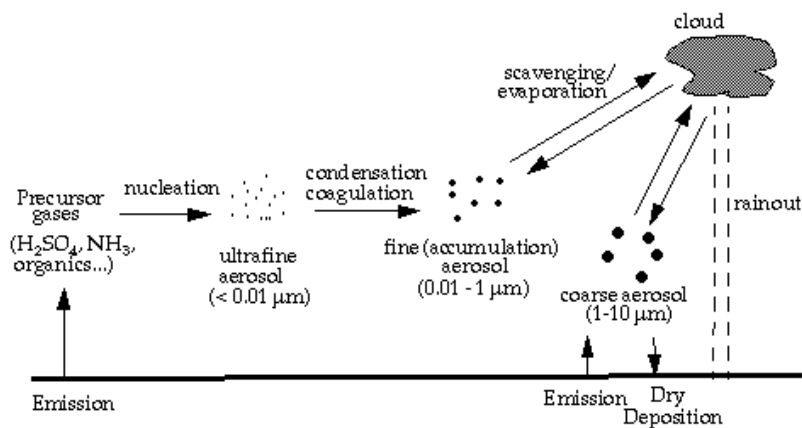


Figure 1: Illustrations of the different processes involved in the production, growth, and eventual removal of atmospheric aerosol particles (source: <http://acmg.seas.harvard.edu>).

The atmosphere is an oxidizing medium. Many environmentally important organic and inorganic compounds are removed from the atmosphere mainly by oxidation (*Kawamura et al., 1996; Pokhrel et al., 2014; Kunwar and Kawamura, 2014*). The most abundant oxidants in the Earth's atmosphere are O₂, O₃ and OH radical. Oxidation in the troposphere is of key importance because the troposphere contains the bulk of atmospheric mass (85%) (see <http://acmg.seas.harvard.edu/>) and because gases are generally emitted at the Earth surface and the Ocean during bubble bursting process and injected to the Atmosphere (*Kawamura et al., 1999, 1996a, 1996b; Pokhrel et al., 2014*). Hence they have two major sources (1) primary and (2) secondary sources. Moreover, based upon the emissions, they have also two major sources (1) biogenic sources, which include biological activities i.e., phytoplankton, virus, bacteria, algae and fungal spores, pollen, fruits, yeast fragments, soil surface, unpaved dust, buds and roots (*Fu et al., 2012, and references therein*) and (2) anthropogenic sources, which can represent industrial activities and/or all types of human activities (*Kawamura et al., 2004*). These sources make very complex geochemical cycle in the atmosphere, land and ocean as shown in Figure 2.

Anything in the atmosphere eventually can end up in an ice core. Some materials are reversibly deposited, but most remain in the ice unchanged. The details of the air-snow transfer process are very complex but are being elucidated. Careful statistical and physical analyses are needed to make sense of small, short lived changes, but large changes in concentrations of most materials in ice reflect changes in their atmospheric loading and atmospheric transport with high confidence. In contrast, there are some limiting factors to know the exact mechanism of productions, destructions and eventual removal of atmospheric aerosol particles for an ice core at a time especially for organic compounds. They can be easily oxidized under solar radiation even in the ambient atmospheric temperature.

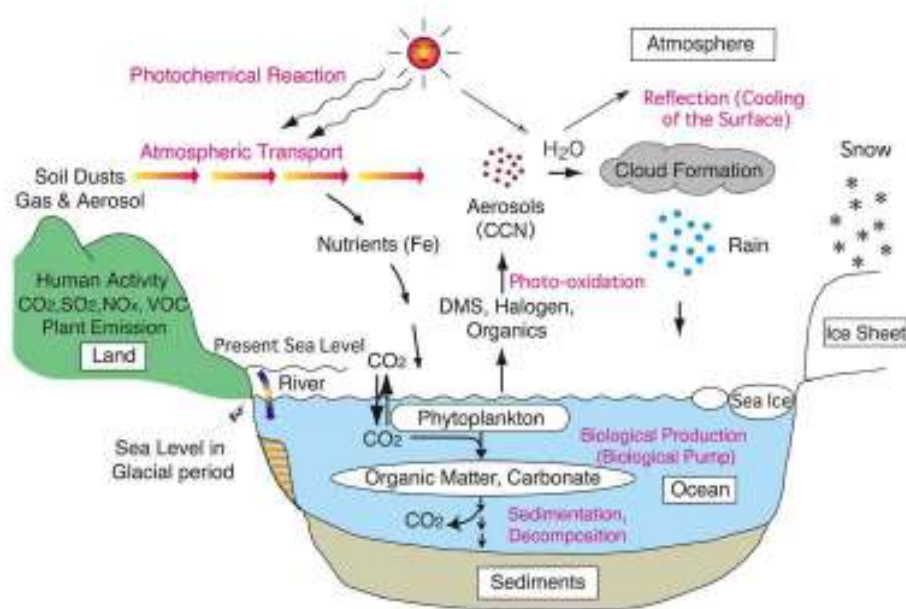


Figure 2: Schematic diagram of the geochemical cycle in the atmosphere, land and ocean (source: <http://environ.lowtem.hokudai.ac.jp/index-e.htm>)

For instance, low molecular weight (LMW) dicarboxylic acids, oxocarboxylic acids and α -dicarbonyls are present as particles in the ambient atmosphere because of their low volatilities, and would have less chance of evaporation than other volatile monocarboxylic acids [Kawamura *et al.*, 2001] from the snow surfaces. In contrast, maleic acids can photo-isomerize to fumaric acid in the snow surface in the presence of solar radiation. Thus, we can assume that LMW dicarboxylic acids, oxocarboxylic acids and α -dicarbonyls could be changed by evaporation, and can be moved out from the snow/air interface and some changes after deposition. These possibilities may be due to sublimation or condensation during snow metamorphism and surface hoar formation, and play important role at least for diamond dust chemical compositions in Arctic regions [Jacobi *et al.*, 2012; Domine *et al.*, 2011]. The rates of atmospheric production, destruction and sinks of these organic compounds in the snow surfaces are not quantitatively well known [Jacobi *et al.*, 2012; Domine *et al.*, 2011; Sumner and Shepson, 1999; Osada and Langway, 1993].

1.4. Aging for an Ice Cores

One of the biggest problems in any ice core study is determining the age-depth relationship. Many different approaches have been used and it is now clear that fairly accurate time scales can be developed for the last 10,000 years where sufficient snow falls each year to form recognizable annual layers, marked by seasonal variations in physical, chemical, electrical, and isotopic properties. These can be counted to determine ages. Accuracy can be assessed by comparison to the chemically identified fallout of historically dated volcanoes and in other ways (*Richard, 2000*).

Prior to that, there is increasing uncertainty about ice age. The problem lies with the fact that the age-depth is highly exponential, and ice flow models are often needed to determine the ages of the deepest sections of ice cores (*Dansgaard & Johnson, 1969*). For example, the upper 100 m of a core may represent 50 years, while the next 50m may span another 100 year time period, due to the compaction, deformation and flow of the ice sheet in question. It seems possible to count annual layers into the glacial period (>100 years ago) and possibly down to 1,000 years. Radio isotope dating, using ^{210}Pb (lead), ^{32}Si (silicon), ^{39}Ar (argon) and ^{14}C (carbon) (*Suzuki et al., 1991; Paterson et al., 1977; references therein*) have all been used with varying degrees of success, over different time scales, to determine the age of ice cores (*Nesje and Dahl, 2000*). For instance, the ice core ages can be determined by annual counting of hydrogen isotopes (δD) and Na^+ seasonal cycles. Using reference horizon of tritium peaks in 1963 and 1964 provided ice age control. By this methods, bottom of ice core sample was estimated to be 343 years old; i.e., 1665 AD for this study (*e.g., Tshushima, 2011; Tsushima et al., 2014*).

1.5. Purpose of this Study

Historical variability of aerosol can be reconstructed from ice core. Although very few studies have been reported for diacids, oxoacids and α -dicarbonyls in ice core [Kawamura *et al.*, 2001], previous studies from Greenland ice core show that historical changes in the concentration and composition of low molecular weight diacids appear to link with decadal scale climate fluctuations in the northern high latitude over the past several hundred years [Kawamura *et al.*, 1999; Kawamura *et al.*, 2001]. However, it is not clear how we can understand the interactions and link between organic aerosols and climate change.

The atmospheric compositions are significantly influenced by long- and short-range atmospheric transport of aerosols and gases, air mass circulation, and direct impact of solar radiation. The continental Arctic air mass transported to lower latitudes like Alaska can lead to the formation of stratocumulus or stratus clouds [Paul *et al.*, 1998; Adams *et al.*, 1992]. Climate in Alaska including the North Pacific and Arctic Ocean is influenced by various types of tropospheric circulation such as Arctic Oscillation (AO), El Niño/Southern Oscillation (ENSO), Pacific Decadal Oscillation (PDO) and Great Pacific Climate Shift (GPCS) [Hartman and Wendler, 2005; D'Aleo and Easterbrook, 2010]. These circulation systems assemble different types of air masses from different climatic locations. Different types of atmospheric circulation deliver various types of organic and inorganic species to the Arctic to control the ambient aerosol compositions.

Similarly, many permanent and semi-permanent low and high pressure centres are present near and around Alaska. For example, Aleutian Low (AL) pressure centre [Harvey and Hitchman, 1996; Harvey *et al.*, 1999], eastern Siberian high pressure system [Parkinson, 1990], and even direct and indirect anticyclonic influences over Alaskan regions [Orsolini *et al.*, 1997] are important factors to control the Arctic climate systems. Such a complex type of Alaskan atmospheric system at times can easily lead to alter the atmospheric processes and

build up new chemical compositions during atmospheric interactions both physically [*Kaspari, et al., 2005, 2007, 2009*] and chemically [*Kawamura and Gagosian 1987; 1990; Kawamura et al., 2001*] under direct and indirect solar radiation followed by photochemical oxidation process in the atmosphere [*Kunwar and Kawamura, 2014, references therein*].

Few studies have been reported for these compounds including biomass burning tracers suggest that historical changes in the concentration and composition of these species appear to link with decadal to multi-decadal temperature variability in the northern high latitude [*Kawamura et al., 1999; Kawamura et al., 2001; Kawamura et al., 2012*]. Although, the interactions and link between organic aerosols and climate change are not clear yet. Hence, we have presented these organic compounds including biogenic secondary organic tracers from isoprene and monoterpenes as well as major ions from the saddle of the Aurora Peak and Kamchatka and discuss the sources and formation process, which are associated with climate oscillations in the North Pacific regions.

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Chapter 2: Ice core records of dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid and α -dicarbonyls from south Alaska: Implications for climate change in the Northern Hemisphere since 1665

1.2. Introduction

Organic aerosols, which are ubiquitous in the atmosphere, have an influence on radiative forcing and thus climate of the Earth directly and indirectly affected by acting as cloud condensation nuclei or ice nuclei [e.g., Ramanathan *et al.*, 2001]. To better understand the role of organic aerosols in the climate system, it is vital to investigate long-term variability of organic aerosol components in the past, which are preserved in ice core and lake, and sea sediments [Kawamura *et al.*, 2001; Seki *et al.*, 2010, 2011] for a long time in the Northern Hemisphere (NH). Dicarboxylic acids, oxoacids and α -dicarbonyls that can be originated from biogenic as well as anthropogenic sources [Grosjean *et al.*, 1978] are major components of water-soluble organic aerosols [Sempéré and Kawamura, 1994, Kerminen *et al.*, 2000].

Although very few studies have been reported for diacids, oxoacids and α -dicarbonyls in ice core suggest that historical changes in the concentration and composition of these low molecular weight diacids (LMDs) appear to link with decadal to multi-decadal scale climate oscillations in the northern high latitude [Kawamura *et al.*, 1999; Kawamura *et al.*, 2001]. However, the interactions and link between organic compounds and climate oscillation is not clear. Here, we report LMDs, ω -oxoacids, pyruvic acid and α -dicarbonyls from the Alaskan region and discuss the sources and formation process which are associated with climate oscillations in the NH.

2.2.1. Site Description

About 180 m long ice core was drilled in the saddle of the Aurora Peak of Alaska (APA), (63.52°N; 146.54°W, elevation: 2,825 m), located southeast of Fairbanks (Figure 1). The ice core ages were determined by annual counting of hydrogen isotopes (δD) and Na^+ seasonal cycles and using reference horizon of tritium peaks in 1963 and 1964 has provided age control. By this methods, bottom of ice core sample was estimated to be 343 years old; i.e., 1665 AD [Tshushima, 2011; Tsushima et al., 2014]. The ice core sample was cut into ~50 cm and direct transported to the laboratory of the Institute of Low Temperature Science (ILTS), Hokkaido University, Japan and stored in a dark cold room (at - 20°C) until analysis.

2.2.2. Chemical Analysis

About 5 mm surfaces of ice core sample were shaved off on a clean bench at - 4°C in a cold room using a ceramic knife to avoid a possibly adsorbed contamination during sample collection and transport to ILTS using the method previously reported [Legrand et al., 1993; Savarino and Legrand, 1998; Kawamura et al., 2001]. These scraped samples were kept for 24 hours in a Teflon container in a standard clean room. The melt water samples were transferred into brown glass bottles, to which mercuric chloride was added to suppress the microbial activity [Kawamura et al., 2001]. Sampling frequency was ~35% of 180 m long ice core in this study; total numbers of ice core sections were 122.

We determined diacids, ω -oxoacids, pyruvic acid and α -dicarbonyls as previously reported [Kawamura et al., 1996a, 2001]. Briefly, 100 ml of melt water were adjusted to pH = 8.5-9.0 using 0.1 M KOH and concentrated in a pear-shaped flask until dryness using a rotary evaporator under vacuum. The dried samples were reacted with ~0.25 ml of 14% boron trifluoride (BF_3)/n-butanol at 100°C for 1 hour. After extraction of derived butyl esters and dibutoxy acetals with n-hexane, derivatives of dicarboxylic acids, oxocarboxylic acids and α -

dicarbonyls were determined using a Hewlett Packard (HP 6890) capillary gas chromatograph (GC). The GC peaks were identified by comparison with GC retention times of authentic standards and confirmed by mass spectral examination using a GC/MS system.

Before the analysis of real ice core samples, recovery test was conducted. 10 μ l authentic standard solution containing free oxalic (C_2), malonic (C_3), succinic (C_4), glutaric (C_5) and adipic (C_6) diacids having 1.03, 1.12, 1.46, 1.04 and 0.83 n moles per μ l, respectively, were spiked to organic free pure water (100 ml), which were analyzed as a real sample. The recoveries were above 88% for oxalic (C_2) and more than 90% for C_3 , C_4 , C_5 and C_6 . We also performed the reproducibility test. The analytical errors in the replicate analysis were 1.6, 2.7, 3.2, 2.4 and 0.41% for C_2 , C_3 , C_4 , C_5 and C_6 , respectively. The laboratory blank levels were on average 3.8, 0.0, 0.8, 0.0, 0.6, and 1.5% of the real samples for C_2 , C_3 , C_4 , C_5 , C_6 and phthalic acid (Ph), respectively. Here, all species concentration has been corrected by subtracting a procedural lab blanks.

2.2.3. Backward Air Mass Trajectories

Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model was used to detect the source regions of air mass. 10-day back trajectory analysis at 500 m above the ground was performed every day during 1989 when we got higher concentrations of organic compounds. We found that all the air parcels were delivered from the ocean (except for 4 days). Moreover, 10 day backward trajectory based on Lagrangian tracking method since 1992-2002 suggested that Alaskan regions can receive significant air masses from adjacent parts of North Pacific Regions, East Asia, Eastern Russia, Siberia, the Okhotsk and Bering Seas, higher latitudes of Alaskan regions, the Gulf of Alaska, Japan, Canada, Arctic Ocean and Europe in the troposphere (>300 hPa) [Yasunari and Yamazaki, 2009; Cahill, 2003].

2.3. Results and Discussion

2.3.1. Correlation Analysis: Possible Sources and Formation Mechanism

We determined more than 30 compounds. Their sources, formation and transformation process are very complex as previously reported elsewhere [e.g., Kawamura *et al.*, 1996a, 2001; Kunwar and Kawamura, 2014a; references therein]. Table 1 shows the results of correlation analyses of diacid species in the APA ice core. We found very strong correlation between oxalic acid (C_2) and its precursor compound malonic (C_3) ($R^2=0.81$) and good correlations between C_2 and glyoxylic acid (ωC_2), 3-oxopropanoic acid (ωC_3), 4-oxobutanoic (ωC_4), methylmaleic (mM) and methylglyoxal (MeGly) are 0.57, 0.54, 0.48, 0.55 (not shown in table), and 0.52 respectively. These correlations suggest that C_2 is formed by the oxidation of its precursors as described in later sections (references therein). Glutaric acid (C_5) is strongly correlated with 9-oxononanoic acid (ωC_9) ($R^2 = 0.79$), and adipic acid (C_6) is with 7-oxoheptanoic acid (ωC_7) (0.77; not shown in table) and azelaic acid (C_9) (0.59). These results suggest that C_5 and C_6 are derived from marine biogenic sources because these ωC_9 and C_9 are a specific biogenic tracer formed by photochemical oxidation of unsaturated fatty acids (e.g., $C_{18:1}$) [Kawamura *et al.*, 2001, references therein]. Pimelic (C_7) is strongly correlated with C_9 (0.74) and oxoacids such as ωC_3 (0.77), ωC_4 (0.70), and ωC_9 acid (0.79).

C_9 also shows strong correlations with 5-oxopentanoic (ωC_5) ($R^2=0.72$), ωC_7 (0.66) (not shown in table) and ωC_9 (0.67). It is to be note that a good correlation was obtained between phthalic (Ph) and ωC_9 (0.59). This correlation between ωC_9 and Ph suggests that phtahalic is of biogenic origin because ωC_9 is an intermediate oxidation product of biogenic unsaturated fatty acids such as oleic acid ($C_{18:1}$), although there may be some anthropogenic input for Ph after the 1980s. The strong correlation between ωC_2 and MeGly (0.75) suggests that they have similar sources and similar reaction pathway [Kunwar and Kawamura, 2014a].

2.3.2. Principal Component Analysis for Selected Organic Compounds

We applied principal component analysis to detect the multiple sources of diacids, oxoacids and α -dicarbonyls [Kunwar and Kawamura, 2014a, references therein] for an ice core ($n = 122$). The strong loadings of glutaric (C_5), adipic (C_6), pimelic (C_7), azelaic (C_9), 4-oxopimelic (kC_7), 5-oxopentanoic (ωC_5), 7-oxoheptanoic (ωC_7) and 8-oxooctanoic (ωC_8) were found in Component 1 (Table 2), suggesting that they are formed by photochemical oxidation of biogenic unsaturated fatty acids. In addition, Component 1 is characterized by high loadings of glyoxal (Gly), methylmalonic (iC_4) and 2-methylglutaric (iC_6), suggesting an oxidation of biogenic organic precursors for these compounds.

Component 2 showed high loadings of C_2 , C_3 , C_4 , oxomalonic (kC_3) and maleic (M) suggesting the photochemical production by the oxidation of precursors compounds such as ω -oxoacids and pyruvic acid as well as aromatic hydrocarbons from biomass burning. In addition, Component 3 showed high loadings of glyoxylic (ωC_2), sebacic (C_{10}) and undecanedioic (C_{11}), which may be associated with biogenic sources including isoprene [Andreae et al., 1987] and unsaturated fatty acids from terrestrial higher plants, marine phytoplankton as well as bacterial activities from the marine atmosphere (e.g., C_{10} and C_{11} : double bond could be oxidized to lower carbon number). High loadings of suberic (C_8), 9-oxononanoic (ωC_9) and phthalic (Ph) acids in Component 4 suggest that source of Ph is biogenic because ωC_9 is the oxidation product of unsaturated fatty acids, although the loading is not very high. Hence, we consider that anthropogenic input of Ph should be minor at least before the 1980s.

2.3.3. Historical Changes in the Concentration of Dicarboxylic Acids

2.3.3.1. Shorter-Chain Diacids: Possible Sources and Formation Mechanism

The production mechanism of oxalic (C_2), malonic (C_3) and succinic (C_4) has been explained by photochemical chain reactions of long chain diacids in ambient aerosols [Carlton *et al.*, 2006, 2007; Legrand *et al.*, 2007]. Dicarboxylic acids in the ambient aerosols can be formed by secondary photochemical reaction of aromatic hydrocarbons [Pavuluri *et al.*, 2010; Talbot *et al.*, 1995; Kunwar and Kawamura, 2014a], cyclic olefins, and unsaturated fatty acids [Ervens *et al.*, 2004; Ho *et al.*, 2011]. The naturally derived organic species may be oxidized to result in mid-chain ketocarboxylic acids, hydroxyacids, C_3 , C_4 and azelaic (C_9) acid [Kawamura *et al.*, 1996b; Kunwar and Kawamura, 2014a]. Moreover, Kawamura and Ikushima [1993] reported that C_2 can be produced by the oxidation of ketomalonic acid (kC_3) as well as malic acid (hC_4) in the presence of OH radicals and pyruvic (Pyr) acid can act as a precursor of C_2 [Lim *et al.*, 2005].

Oxalic acid (C_2) was found as the most abundant species followed by adipic acid (C_6), succinic (C_4), phthalic (Ph) and azelaic acid (C_9). The molecular distribution is different from that of south Greenland ice core [Kawamura *et al.*, 1999], where C_4 is the most abundant diacid. Relative abundances of C_2 , C_6 , C_4 , C_9 , and Ph comprised 30, 9.3, 16, 7.6 and 8.2% of total diacids, respectively (not shown in Table). C_2 , C_3 and C_4 showed somewhat similar historical trends with common peaks in 1690s, 1780s, 1840s-1850s, and 1980s-2008 (Figure 3b,c,d). The higher spikes of C_2 , C_3 and C_4 are consistent with those of kC_3 and hC_4 (Figure 4i, j), suggesting that C_2 is formed from the oxidation of C_3 and C_4 because kC_3 and hC_4 are the intermediate compounds. This ice core study showed that C_2 is most abundant diacid in most ice sections (5.69 - 180 meter in depth).

Figure 3b shows that there are many sporadic peaks of C_2 in 1695 (14.6 ng/g), 1764 (13.5 ng/g), 1786 (15.2 ng/g), 1794 (11.3 ng/g), 1840 (14.5 ng/g), 1846 (16.1 ng/g), 1851 (8.34

ng/g), 1913 (10.24 ng/g), 1966 (17.1 ng/g), 1999 (27.9 ng/g) and 2005 (12.9 ng/g) compared to its background level since 1665-2008 (range: 2.01-27.8, ave. 7.17 ± 4.18). Average concentrations since 1665-1860, 1861-1979 and 1980-2008 are 7.92, 6.42 and 7.03 ng/g-ice, respectively (Table 3). We detected higher spikes of levoglucosan (biomass burning tracer- lignin coal combustion, broad-leaf trees and conifer trees, e.g., Simoneit, 2002) and dehydroabietic acid from the same ice core in these periods (except for 1840, 1846 and 1851). In contrast, there is a weak correlation (R) of levoglucosan with dicarboxylic acids, e.g., C₂ (0.56) and C₃ (0.38), oxocarboxylic acids, e.g., ω C₂ (0.20), Pyr (0.25) and α -dicarbonyls, e.g., Gly (0.09) and MeGly (0.27). Similarly, correlations (R) of dehydroabietic (conifer resin) and vanillic acid (incomplete combustion of boreal conifer trees) with these compounds are less than 0.11, suggesting that precursor compounds of end product of dicarboxylic acids could not be seriously influenced by biomass burning [Kawamura *et al.*, 2013; Kunwar and Kawamura, 2014a; Kundu *et al.*, 2010; Savarino and Legrand, 1998]. Concentrations of C₂ in this study are several times higher than those of Greenland Site-J ice core (range: 0.36 - 10.7, av. 2.10 ng/g-ice) [Kawamura *et al.*, 2001]. Kang *et al.* [2001] reported 180-year record of oxalate in Mt. Everest ice core with average concentration of 13.7 ng/g-ice. Savarino and Legrand [1998] reported lower concentrations (1-20 ng/g) of oxalic acid in Greenland ice core, which they considered to be heavily influenced by biomass burning.

The concentration ratios of atmospheric organic compounds can be used to examine the origin of these atmospheric tracers, atmospheric oxidation, source and sinks for the aerosol [Smyth *et al.*, 1996; Ho *et al.*, 2010; Wang *et al.*, 2011; Kunwar and Kawamura, 2014a, b]. It should be noted that concentration ratios of C₂/C₃, C₂/C₄ (Figure 6a, b) and C₃/C₄ (not shown in figure) are somewhat increasing since the 1800s, suggesting that photochemical oxidation process has been enhanced. High average ratios of C₂/C₃ (range: 1.6 - 230, av. 18), C₂/C₄ (0.73 - 8.5, 2.4), C₃/C₄ (0.04 - 3.4, 0.25), C₂/ ω C₂ (1.6 - 220, 19), C₂/Pyr (0.12 - 390, 9.8) and C₂/Gly

(3.2 - 230, 54) suggest that C_2 is produced by the oxidation of its precursor compounds [Kunwar and Kawamura, 2014a; Ho et al., 2011; Wang et al., 2006; Miyazaki et al., 2009].

4-Oxobutanoic acid (ωC_4) can be derived by the oxidation of unsaturated fatty acids containing a double bond at C-4 position, which can be further oxidized to C_4 [Kawamura et al., 1996b]. We found that the historical variation of major peaks of C_4 are similar to ωC_4 (Figure 3d, 5d) with sporadic peaks in 1695 (14.9 ng/g), 1750 (9.38 ng/g), 1764 (9.06 ng/g), 1786 (16.2 ng/g), 1840 (9.78 ng/g), 1846 (12.8 ng/g), 1851 (5.60 ng/g) and 1913 (8.58 ng/g) than its background level (range: 0.36-16.2, ave. 4.3 ± 3.2 ng/g-ice) since 1665-2008 (Table 3). Decreasing trend of C_4 indicates the increased photochemical oxidation of C_4 with respect to temperature. For instance, relations between 5 points running mean (5-RM) of extra tropical northern Hemispheric temperature (ET), i.e., 5-RM ET [e.g., Wilson et al., 2007] and 5-RM of C_2/C_4 (0.83) and C_2/C_3 (0.71) are positive (see Figure 6a, b and d). It should be noted that C_3 is hardly derived from the oxidation of aromatic hydrocarbon (Figure 3c). The intermediate compounds between C_2 , C_3 and C_4 , i.e. ketomalonic (kC_3) and malic (hC_4) also showed positive correlations with respect to this temperature (ET). These result further suggest that there could be decreasing marine sources and/or increased photochemical oxidation (e.g., C_4 could be oxidized to C_3 and/or C_2). Meanwhile, snow accumulation rate of this sampling site (8 mm year^{-1}) is increasing since 1900 and then abrupt change (23 mm year^{-1}) around 1976 (e.g., Tsushima et al., 2014). In contrast, C_4 showed lower concentration since 1900-2008, suggesting that the concentrations may be independent to the snow accumulation, being similar to Dome C and other studies of Antarctica, in which NO_3^- is independent to the snow accumulation rate [Legrand and Kirchner, 1990; Legrand and Delmas, 1986, 1988].

2.3.3.2. Longer-Chain Diacids: Possible Sources and Formation Mechanism

Adipic acid (C₆) can be derived from anthropogenic cyclohexene and biogenic unsaturated fatty acids via photochemical oxidation [Kawamura *et al.*, 1996b; Kawamura and Gagosian, 1987]. Among the longer chain diacids (C₅ to C₁₁), C₆ is the most abundant followed by azelaic (C₉) and suberic (C₈). C₆ showed spikes in 1695 (60.1 ng/g), 1702 (11.0 ng/g), 1718 (14.0 ng/g), 1840 (57.0 ng), 1846 (14.8 ng/g), 1851 (22.0 ng/g), 1983 (19.9 ng/g), 1989 (30.09 ng/g), 1991 (13.7 ng/g), 1992 (10.5 ng/g) and 1999 (19.8 ng/g) compared to its background level concentration (range: BDL-60.1, ave. 4.99 ± 10.5 ng/g-ice). The historical trend of C₆ in 1680s -1840s is somewhat similar with those of glutaric (C₅) and pimelic acid (C₇) (except for few point) and many peaks are similar to C₈, C₉ and sebacic acid (C₁₀).

It is meaningful to compare the historical variations of C₅ (except for 1950s), C₆, C₇, C₈, and phthalic (Ph) with C₉, which is a specific photochemical oxidation product of biogenic unsaturated fatty acids (e.g., C_{18:1}, C_{18:2} and C_{18:3}) [Kawamura and Gagosian, 1987].

Unsaturated fatty acids are produced by sea surface microorganisms such as phytoplankton and emitted to the atmosphere via bubble bursting process of sea surface micro layers [Sempéré and Kawamura, 1996; Marty *et al.*, 1979]. We found that many higher spikes of C₅, C₆, C₇ and C₈ are similar with that of C₉, with correlations between C₆ and C₉ and/or ω C₉ (Table 1), and principal component analyses (Table 2) suggesting that the source of C₆ is marine biota rather than continental pollutants. Kawamura *et al.* [2001] also discussed biogenic sources of C₆ in Greenland Site-J.

Azelaic acid (C₉) showed many sporadic peaks around 1688 (5.98 ng/g), 1702 (5.52 ng/g), 1728 (4.98 ng/g), 1738 (4.36 ng/g), 1764 (4.75 ng/g), 1840 (9.61 ng/g), 1846 (8.10 ng/g), 1851 (8.35 ng/g), 1983 (11.83 ng/g), 1989 (10.3 ng/g), 1990 (8.37 ng/g), 1991 (9.96 ng/g), 1992 (10.2 ng/g), 1994 (6.91 ng/g) and 1999 (7.85 ng/g) compared with its background level since the 1660s (range: 0.16-11.8, ave. 2.65 ± 2.95 ng/g-ice). The enhanced concentrations of C₉

during 1680 – 1770, 1840s, 1890 - 1920 and 1980 - 2000s (Figure 3i) suggest more contributions of unsaturated fatty acids and photochemical oxidation in the air and/or on snow surface [Kawamura *et al.*, 1996b, 2001]. This variability of C₉ concentrations may be associated with past changes in the retreat/advance of sea ice [Kawamura *et al.*, 1999] in the oceanic areas adjacent to Alaska and subsequent emission of unsaturated fatty acids from the ocean surface [Kawamura *et al.*, 1999, 2001; Barger and Garrett, 1970, 1976]. For instance, Volz and Kley [1988] reported a long-term increase of ozone level in rural areas of the Northern Hemisphere over the past century, indicating an increased oxidizing capability of the atmosphere.

Miller *et al.* [2007] confirmed the decline of sea ice cover by 3 to 4% in the Arctic Ocean from 1980 to 2000. This can increase the sea air interaction and emissions of unsaturated fatty acids followed by the increase in the atmospheric oxidizing capability [Kawamura *et al.*, 2001]. It may cause the enhanced concentrations of C₉ and can be applied to other dicarboxylic acids during these periods of 1680s - 1800, 1840s, 1890 - 1920 and 1980 - 2000s. It should be noted that the atmospheric pressure is most significantly declined over the Gulf of Alaska, when Arctic sea ice declines [Budikova 2009]. Thus, Aurora Peak can receive more air masses containing these compounds from the adjacent areas (e.g., the Gulf of Alaska) of marine atmospheric low-pressure system [Yasunari and Yamazaki, 2009]. It will be more discussed in later sections. It is reasonable to see the historical trends of sebacic (C₁₀) and undecanedioic acid (C₁₁). C₁₀ and C₁₁ are produced by the oxidation of unsaturated fatty acids such as vaccenic acid (C_{18:1}ω₇), which is abundantly present in the sea surface micro layers, where bacterial activity is important and emitted to the atmosphere followed by photochemical oxidation [Kawamura and Gagosian, 1987]. The profiles of C₁₀ and C₁₁ are different than those of other longer chain diacids species (Figure 3j, k). They showed good correlations with marine tracers (e.g., C₁₀ has R= 0.72 with C₉). Particularly, C₁₁ showed completely different

historical trend, suggesting that the marine bacterial activities can alter the distribution of longer chain diacids via photochemical oxidation.

2.3.3.3. Branched Chain Saturated and Unsaturated Dicarboxylic Acids

Among the branched chain saturated diacids (iC₄, iC₅ and iC₆), methylmalonic (iC₄) showed the highest concentration (Table 3). Historical trend of iC₄ is similar with those longer chain diacids (e.g., C₅ - C₈) and somewhat similar with 2-methylglutaric acid (iC₆). We also found somewhat higher concentrations of iC₄, methylsuccinic (iC₅) and iC₆ during the periods (e.g., 1690s, 1710s, 1750s, 1790s, 1840s, 1850s and 1890s) (Figure 4a, b and c), when azelaic (C₉) showed peaks (Figure 3i), suggesting that similar source of C₉ could be activated.

Fumaric acid (F) showed higher concentrations than maleic (M) and methylmaleic (mM) among the aliphatic unsaturated diacids (i.e., M, F and mM) since 1665-2008 (Table3). Fumaric is formed by the photo-isomerization reaction of cis isomer, i.e., maleic acid (M), which can be formed by the oxidation of aromatic structures such as phthalic acid (Ph) [Kunwar and Kawamura, 2014a]. Except for some points, F is more abundant than M. The concentrations of these unsaturated diacids (ave. 0.15, 0.32 and 0.30 ng/g-ice for M, F and mM, respectively) are higher than those (av. 0.10, 0.08, and 0.023 ng/g-ice for M, F and mM, respectively) reported in Greenland Site-J ice core [Kawamura *et al.*, 2001]. In addition, Matsunaga *et al.* [1999] reported the average concentrations of M and F (av. 0.74 and 0.32 ng/g, respectively) for fresh snow at Dome Fuji, Antarctica from 1995 to 1996, which have been interpreted to have local contamination of fossil fuel combustion products from the Dome Fuji base. Ratio of F to M (i.e., F/M) has significantly high values (range: BDL-30.0, ave. 3.33 ±6.41). The correlation of annual total solar irradiance (STI) [Lean, 2000] with 30-RM of F/M (except for 3 points) is strong (R = 0.83) and correlation of 30-RM of F/M with 30-RM of ET (Figure 6f) is also strong (0.88), suggesting that a significant isomerization reaction occurred.

2.3.3.4. Aromatic and Multifunctional Diacids: Possible Sources and Formation

Mechanism

Phthalic acid (Ph) was detected as the only aromatic diacid (range: BDL-27.7, ave. 3.24 ± 5.21 ng/g). Iso- and tere-phthalic acids that are emitted from plastic burning [Kawamura and Pavuluri, 2010] were not detected at least as major components. Phthalic (Ph) acid showed spikes in 1702 (5.57 ng/g), 1728 (4.64 ng/g), 1840 (27.7 ng/g), 1846 (24.9 ng/g), 1851 (8.02 ng/g), 1983 (8.06 ng/g) and 1989 (21.1 ng/g), 1990 (12.8 ng/g), 1998 (8.68 ng/g), 1999 (11.9 ng/g), and 2000 (9.31 ng/g) compared to its background level (Figure 4g). Average concentration of Ph (0.91 ng/g-ice) is three and six times lower after industrial revolution since 1861-1979 compared to its average concentration since 1665-2008 (3.24 ng/g-ice) and since 1980-2008 (5.55 ng/g), respectively (Table 3). The average concentration of Ph in this study is five times higher than that (av. 0.56 ng/g) from Greenland Site-J ice core [Kawamura et al., 2001]. The historical trend of Ph (Figure 4h) resembles that of marine biogenic sources. Moreover, correlation of Ph with biogenic tracer (ωC_9) is positive ($R = 0.76$) (Table 1).

The sources of Ph may be phenolic compounds that are present in sea surface slicks [Kawamura et al., 2001; Carlson et al., 1988; Carlson, 1982a; 1982b] and emitted to the atmosphere by bubble bursting process [Marty et al., 1979] rather than anthropogenic sources at least before 1980s. For instance, significant concentration of Ph has been detected in aerosols collected at the tropical region, southeast coast of India as a biogenic signature (e.g., phenolic compounds from marine sources) [Pavuluri et al., 2010]. Among the multifunctional diacids (hC_4 , kC_3 and kC_7), malic acid (hC_4) showed the highest concentration (range: BDL-5.96, ave. 0.63 ± 1.24 ng/g-ice), followed by 4-oxopimelic (kC_7) acid (range: 0.01-2.34, ave. 0.24 ± 0.41 ng/g-ice) and oxomalonic (kC_3) acid (range: 0.03-0.77, ave. 0.18 ± 0.16 ng/g-ice), which are intermediate compounds [Kawamura et al., 1996]. Oxomalonic (kC_3) and 4-oxopimelic (kC_7) have been reported, for the first time, in ice core. Historical trends,

correlations (e.g., hC_4) and principal component analysis (e.g., kC_3) suggest their biogenic sources via photochemical oxidation.

2.3.3.5. ω -Oxoacids and Pyruvic Acid: Possible Sources and Formation Mechanism

We detected significant concentration of glyoxylic acid (ωC_2) in all ice core sections, which can be derived from glyoxal (Gly), methylglyoxal (MeGly), maleic (M), methylmaleic (mM) and fumaric (F) acid [Kunwar and Kawamura, 2014a]. It shows higher spikes in 1695 (4.72 ng/g), 1840 (3.40 ng/g), 1846 (1.53 ng/g) and 1851 (1.53 ng/g) than its average concentration since 1665 -1860 (ave. 0.90 ng/g). Similarly, it shows higher peaks in 1989 (2.16 ng/g), 1990 (2.53 ng/g), 1991 (2.41 ng/g), 1992 (3.45 ng/g), 1994 (4.44 ng/g), 1997 (3.81 ng/g) and 1999 (3.58 ng/g) than its average concentration since 1980-2008 (ave. 1.61 ng/g). Moreover, precursor compounds of ωC_2 (e.g., Gly and MeGly) showed higher spikes during biomass burning periods (e.g., 1695, 1702, 1716, 1728, 1786, 1860, 1989, 1991, 1997, 1998, 1999, 2000 and 2006).

Interestingly, there are a weak correlation of ωC_2 ($R = 0.20$ and 0.10) and its precursor compounds, e.g., M (0.32 and 0.03), mM (0.31 and 0.03), Gly (0.09 and 0.03) and MeGly (0.27 and 0.06) with levoglucosan and dehydroabietic acid, respectively, from the same ice core (mutual ice core sections (n) = 118). Correlations with levoglucosan suggest that ωC_2 could be some what influenced from biomass burning and other sources (e.g., correlation of ωC_2 with MeGly is strong; Table 1) during these periods. On the other hand, ωC_4 shows higher average concentration than standard deviation (SD) during these intervals of 1665-1860 (ave. 1.10 ± 0.92), 1861-1979 (ave. 0.36 ± 0.28 ng/g) and 1980 -2008 (ave. 1.64 ± 1.30 ng/g). Decreasing historical trend of ωC_4 (Figure 5d) is similar to malonic (C_3) and succinic (C_4) acid (Figure 3c, d) suggests the similar source of C_3 , C_4 and ωC_4 [Kawamura et al., 1996b, 2001].

The predominance of 9-oxononanoic (ωC_9) acid (range: 0.01-541, ave. 1.13 ± 1.22 ng/g),

which is followed by 4-oxobutanoic (ωC_4) (0.01-4.68, ave. 0.99 ± 1.12 ng/g) and glyoxalic (ωC_2) (range: 0.03-4.72, ave. 0.93 ± 1.05 ng/g) since 1665-2008 (Table 3). Similarly, the relative abundances of ωC_9 , ωC_4 and ωC_2 in total annual oxoacids (ωC_2 - ωC_9) on average comprised 23, 20 and 18 % (not shown in table), respectively. In contrast to this study, ωC_2 of Greenland ice core is more abundant than ωC_9 [Kawamura *et al.*, 2001]. We found, for the first time, the predominance of ωC_9 among ω -oxoacids in ice core and aerosol studies (*e.g.*, Kawamura *et al.*, 1996b, 1999; Kunwar and Kawamura, 2014a). Standard deviation (SD) of ωC_9 is higher than average annual mean in over all period since 1665-2008 (ave. 1.13 ± 1.22 ng/g-ice) as well as during 1861-1979 (ave. 0.59 ± 0.78 ng/g-ice). In contrast, periodic SD since 1665-1860 (ave. 1.64 ± 1.51 ng/g-ice) and 1980-2008 (ave. 1.11 ± 0.80 ng/g-ice) are lower than average concentration (Table 3). It shows higher peaks in 1716 (3.68 ng/g), 1764 (11.2 ng/g), 1772 (4.70 ng/g), 1778 (3.35 ng/g), 1794 (2.35 ng/g), 1802 (2.76 ng/g), 1840 (3.71 ng/g), 1846 (2.29 ng/g) and 1851 (2.08 ng/g) than its average concentration since 1665-1860 (ave. 1.64 ng/g).

Similarly, it showed spikes in 1856 (2.42 ng/g), 1861 (1.99 ng/g), 1865 (1.99 ng/g), 1870 (2.65 ng/g) and 1966 (1.58 ng/g) than its background level concentration since 1861-1979 (ave. 0.59 ng/g). Moreover after 1970s, it showed spikes in 1983 (1.62 ng/g), 1988 (1.83 ng/g), 1889 (3.03 ng/g), 1990 (1.62 ng/g), 1991 (1.53 ng/g), 1997 (1.62 ng/g), 1998 (1.83 ng/g), 1999 (3.19 ng/g) and 2001 (1.63 ng/g) than its average concentration since 1980-2008 (ave. 1.11 ng/g). All these spikes are statistically (t-test) significant ($p=0.000$) since 1665-2008. It should be noted that, $C_{18:1}$ can be oxidized to ωC_9 and/or C_9 [Kawamura and Gagosian, 1987] and relation between azelaic acid (C_9) and oleic acid ($C_{18:1}$) from the same ice core is positive ($R=0.74$). These result suggests a significant contribution of precursor compounds (*e.g.*, $C_{18:1}$) are enriched in the sea surface micro layers and emitted to the atmosphere by bubble bursting process followed by atmospheric oxidation in the source regions [Kawamura *et al.*, 2001;

Kunwar and Kawamura, 2014a]. In fact, we detected very high concentrations of oleic acid ($C_{18:1}$) in the same ice core (e.g., *Pokhrel et al., 2014*).

Pyruvic acids (Pyr) can be produced by photochemical oxidation of aromatic hydrocarbons and o-cresol ($CH_3C_6H_4(OH)$) [*Grosjean, 1983*] and isoprene emitted from biogenic sources [*Andreae et al., 1987*]. Methylglyoxal (MeGly) is also oxidized to result in Pyr [*Carlton et al., 2006, 2007*]. Malic acid (hC_4) can be decomposed by microbes and oxidized to Pyr [*Beijerinck, 1916*]. Pyruvic (Pyr) showed somewhat similar higher spikes with glyoxal (Gly) and MeGly except for 1860s - 1910s (Figure 5i, 5j and 5k). These compounds (Pyr, Gly and MeGly) could be derived from similar sources and similar reaction pathways because they are photochemical oxidation products of organic precursors such as isoprene and/or in-cloud isoprene oxidation and biomass burning activities [*Andreae et al., 1987; Talbot et al., 1995; Lim et al., 2005; Carlton et al., 2006, 2007*]. For instance, recently, nighttime maxima of pyruvic acid was found in aerosol samples from Mt. Tai in central East China due to the enhanced oxidation of methylglyoxal (MeGly) [*Kawamura et al., 2013*].

The average total annual concentrations of Pyr during 1665-1860 (ave. 1.37 ± 1.21 ng/g), 1861-1979 (ave. 1.37 ± 0.82 ng/g), 1980-2008 (ave. 1.59 ± 0.84 ng/g) and total annual average concentration (ave. 1.43 ± 0.97 ng/g) since 1665-2008 are close each other (Table 3). Moreover, relations between 30-RM of Pyr ($R=0.81$) and 30-RM of Gly (0.69) with 30-RM of extra tropical Northern Hemispheric annual temperatures (30-RM ET) observed in the instrumental record (Figure 6d) since 1750-2000 (e.g., *Wilson et al., 2007*) are positive. Similarly, correlations of Pyr ($R=0.25$), Gly (0.09) and MeGly (0.27) with levoglucosan and/or dehydroabietic/vanillic acid are weak. These relations further suggest that emission and degradation of Pyr and somewhat Gly and MeGly are likely to be linked with climate change.

2.3.3.6. α -Dicarbonyls: Possible Sources and Formation Mechanism

Glyoxal (Gly) can be produced by photooxidation of aromatic hydrocarbons such as benzene, toluene, xylene and alkenes and p-xylene [Volkamer et al., 2001, 2006; Rogge et al., 1991, 1998]. Methylglyoxal (MeGly) is also an intermediate product of isoprene, and is further oxidized to oxalic acid (C₂) in aqueous phase [Lim et al., 2005; Warneck et al., 2003; Ervens et al., 2004]. Figures (5j, k, l) showed that there are sporadic peaks since 1665-1860, which are similar to biomass burning periods (see section 3.3.5, e.g., 1695, 1702, 1716 and 1786). Historical trends of these compounds are increasing since 1950-2008 suggesting the SOA formation in the atmosphere [Kawamura et al., 1996b, 2001; Kunwar and Kawamura, 2014a] during the cloud formation process over and around the Alaskan regions may be due to climate change variability (e.g., Gly showed positive correlation with ET).

Briefly, historical records of these compounds (i.e., above all sections) fascinate the pristine climate condition corresponding to forest fires activities, are imprinted in this study. For instance, forest fires intensity before the 1860s (higher spike periods of these diacids and levoglucosan are common) could be in drought seasons by lightning in the Siberian regions and/or Alaskan regions as well as extensive burning to clear land for agriculture purpose in the northern Hemisphere [Whitlow et al., 1994, reference therein]. Suppressing of concentrations trends (except few compounds e.g., Pyr) showed that source could be changed significantly and/or forest fire activities could be suppressed/controlled since the 1860s-1970s [Whitlow et al., 1994]. It should be noted that mid to late 1800s are considered to be the Little Ice Age [Mayewski et al., 1993].

Recent increase of the concentration trends since the 1980s could be climate driven [Miller et al., 2007; Parkinson and Cavalieri, 2002; Parkinson et al., 1999; Whitlow et al., 1994;] including all types of human activities in the source regions. This can be explained various ways. For instance, there is a reduction of sea ice extent at a rate of -2.7 ± 0.5 % per decade, in

which summer rate is greater (-4.9 ± 1.5 %) compared to winter season (-1.8 ± 0.6 %), which is reported by using a 21-year microwave data set of Arctic regions [Parkinson and Cavalieri, 2002]. Such type of sea ice extent declination from 1978 to 2010 for the Northern Hemisphere is further confirmed by other research agencies like National Snow and Ice Data Center (nsidc.org) and/or Alaska Ocean Observing System (www.aos.org). Following the declined sea ice extent in the Arctic region, we observed a distinct increase since the 1980s.

Hence, above all results and discussion demonstrate higher spikes of these diacids (Figure 3-5) around the 1840s (e.g., 1840, 1846 and 1851) and other decades including 1880-1920 (i.e., C₄, C₉, C₁₀, iC₅, kC₃ and Pyr) suggesting the extra point sources and/or local biogenic sources (e.g., terrestrial and marine atmosphere) could be more activated. For instance, Greenland ice core showed comparatively higher MSA during 1840-1850s and 1880-1900 and lower concentration in 1870-1880 [Legrand and Mayewski, 1997; references therein], which is similar to historical trends of azelaic (C₉) acid (Figure 3i). Enhanced emission of MSA during these periods may be due to El Nino years, which can easily drive the higher sea surface wind speeds and/or increase the air-sea exchange of DMS in the Arctic marine environment [Legrand and Mayewski, 1997; references therein]. Another explanation of this higher MSA is sea-ice extent (rotting sea ice), because higher biogenic emissions are occurred in lower latitudes compared to higher latitudes between 50° and 85° during El Nino years [Bates et al., 1992; Legrand and Mayewski, 1997].

2.3.4. Contributions of Diacids and Related Compounds to WSOC

The contributions of total diacids, oxoacids and α -dicarbonyls in WSOC ranged from 0.01 - 6.8% (av. 0.90 ± 1.4 %), 0.00 - 2.2% (0.28 ± 0.43 %), and 0.0 - 0.35% (0.04 ± 0.07 %), respectively. Figure (7a, b and c) show similar historical trends of total diacid-C/WSOC (%), total ketoacids-C/WSOC (%) and total α -dicarbonyls-C/WSOC (%) with large peaks in 1730s

and since the 1860s, suggesting that these water-soluble organic compounds are derived from similar sources. Moreover, historical variation of undecanedioic (C_{11}), azelaic (C_9) and adipic (C_6) are similar each other as well as pimelic (C_7), suberic (C_8) and sebacic (C_{10}) (not shown as a figure). These results suggest that diacids, oxoacids and α -dicarbonyls are derived from similar biogenic sources from the ocean [Kawamura *et al.*, 2001]. This is very likely because the North Pacific, Bering Sea and Arctic Ocean surround Alaska.

In contrast, there is a few in-consistency for higher peaks among diacids probably due to different sources of organic aerosols since the 1990s. Similarly, all oxoacids showed similar trends with 9-oxononanoic (ωC_9) (not shown as a figure), suggesting that oxoacids are derived from the oxidation of biogenic unsaturated fatty acids. Interestingly, ωC_9 showed a similar trend with azelaic (C_9) (except for 1665 to 1700s). This result suggests that the formation process and source of C_9 and ωC_9 are similar. The similar trends between shorter diacids and oxoacids suggest that most of the diacids are formed by the oxidation of oxoacids. Similar trends of glyoxal (Gly) and methylglyoxal (MeGly) and pyruvic (except for 1840s) suggest that they are derived from biogenic volatile organic compounds (BVOCs) including isoprene.

We found that historical fluctuations in the ratios of diacid-C/WSOC, oxoacids-C/WSOC and α -dicarbonyls-C/WSOC (Figures 7a, b, c) are somewhat similar with the extra tropical Northern Hemispheric temperature departures (Figure 6f) after 1860s to present time (*e.g.*, Wilson *et al.*, 2007) and historical trend of δD Kamchatka (Figure 7d) ice core records [Sato *et al.*, 2014]. Historical trends of δD Kamchatka designate the extra tropical North Pacific surface climate conditions (Sato *et al.*, 2014; Smith *et al.*, 2008) and signify the variations of climate oscillation such as Pacific Decadal Oscillation (PDO) and North Pacific Gyre Oscillation (NPGO), which may have caused an increased atmospheric oxidizing capability.

2.3.5. Response of Ice Core Organic Tracers to Non Periodic Events

Holdsworth et al. [1996] reported higher concentration of black carbon during 1800-1810, 1850-1950 in the Mount Logan as a source of natural biomass burning from Canada, Alaska, Siberia and “Pioneer Agriculture Revolution (PIAGREV)”. GISP2 ice core showed higher concentration of insoluble micro particles around 1850-1870s, 1885-1900, 1910-1920 reflect an increase in atmospheric turbidity during PIAGREV could be due to “clear-cutting”, biomass burning and tilling of top soil (Holdsworth et al., 1996, references therein). Concentrations of NH_4^+ , which is also an indicative of biomass burning, increased at the site of GISP2, 20D and Mount Logan [Holdsworth et al., 1996]. Savarino and Legrand [1998] showed that central Greenland Summit was influenced from forest fires during 1850 - 1900s. Large forest fires would have enriched oxalate, together with other organic acids and ammonium in the ice sheet layers [Legrand et al., 1992; Legrand and Angelis, 1995, 1996] and aerosols samples [Andreae, 1988; Lefer, 1994; Holdsworth et al., 1996]. It should be noted that non-fossil fuel sources were active during the last quarter of the nineteenth century [Stanhill, 1982].

Relatively low concentrations (Figure 3, 4 and 5) were observed in this study site since 1860s - 1970s suggesting that there was completely different sources of air masses (may be local biogenic emission rather than regional emission), which could be activated around southern Alaska. Moreover, we got higher concentrations around 1988-1989 (Figure 8a) for all species and from backward trajectory analysis we found that all the air parcels (except 4 days) were come from Pacific Ocean. In addition, East Asian air masses should be mixed with other air masses from the ocean by the Arctic atmospheric circulation [Yasunari and Yamazaki 2009; Cahill, 2003] and extreme meridional airflow from mid-latitudes to Alaskan regions [Brown et al., 2010]. These situations would cause the elevated atmospheric concentrations of diacids.

2.3.6. Response of Ice Core Organic Tracers to Lower Tropospheric Temperature

The present ice core study shows that mean deviation of concentrations of total dicarboxylic acids, oxocarboxylic acids and α -dicarbonyls are increasing by 19, 35 and 18%, respectively, for the period of 1979 - 2008 compared to 1665 - 1978. The concentration trends of all these compounds are similar each other since the 1980s and some what similar with the satellite-derived global tropospheric lower temperature anomalies (T) for 1979 - 2000 (from surface to ~ 6 km) using microwave soundings units flying aboard NOAA'S TIROS-N weather satellites (Figure 8a, b). In addition, we found positive correlations between these compounds and temperature (T). For instance, relation between relative abundance of oxalic acid, i.e. end product of diacids (except for 1980, 1993 and 1993) with is positive ($R = 0.74$).

Moreover, relation between dicarboxylic acids, e.g., 9 points running mean (RM) of C_2 (9-RM C_2) (0.77), and 9-RM of C_4 (0.74), oxocarboxylic acid e.g., 9-RM of Pyr with 9-RM of T (0.81) are positive. Similarly, relation of oleic acid ($C_{18:1}$) with extra tropical Northern Hemispheric temperature (ET) (0.83) and C_9 (0.74) showed positive. It should be noted that ET has positive correlations with short chain diacids (e.g., section 3.3.1 and 3.3.5), which is correlated with more than 25 different tree ring proxy records of the world, e.g., European Alps (0.67), western Siberia (0.61), Mongolia (0.70), Nepal (0.49), Northern Yukon (0.60), Wrangell Mountains (0.60), British Columbia (0.77), Idaho (0.41) and Northern Quebec (0.42) (Wilson et al., 2007, references therein). In addition, 1860s -1970s, we detected lower concentrations of these compounds. During these periods, interior Alaskan regions show somewhat a decreasing trend in the reconstructed summer temperature [Barber et al., 2004]. These relations suggest that production and degradation of these compounds, which are associated with oxidizing capacity of the atmosphere, could be controlled by similar meteorological factors (i.e., Climatic Windows) and multi-decadal atmospheric oscillations in the NH.

In contrast, pyruvic (Pyr) and ω C₉ showed different trends (Figure 5h and i). This may be explained by enhanced production of organic precursors such as isoprene and/or in cloud isoprene oxidation [Carlton *et al.*, 2006, 2007; Lim *et al.*, 2005; Talbot *et al.*, 1995] for Pyr and oxidation of unsaturated fatty acid (e.g., C_{18:1}) for ω C₉ and/or C₉ that could be associated through the short-range atmospheric transport from under ample advection of more heat from the Pacific Ocean, Gulf of Alaska, as well as other local and/or point sources of terrestrial biogenic emission, which may have been significantly activated around Alaskan regions during this periods rather than long-range atmospheric transport. For example, intensification of the Aleutian Low can easily provide advection of more heat to the higher latitudes of Alaskan regions [Hartman and Wendler, 2005; Trenberth and Hurrell, 1994]. Moreover, correlations between azelaic acid (C₉) with ω C₉ (0.81) and C₉ with unsaturated fatty acid, e.g., oleic acid (C_{18:1}) is 0.74 and correlations between Pyr, Gly and MeGly with extra tropical Northern Hemispheric temperature (ET) are positive (section 3.3.5) favors the atmospheric oxidation following the air-sea-land interaction, which may govern many factors such as “Climatic Windows”. This quick and complex response on oxoacids (e.g., Pyr) in the Alaskan regions may be a potential research topic in the future.

Annual records of solar total irradiance (STI) showed Damman minima after 1860s (Figure 4m), this consequence can be observed for longer chain diacids and other related compounds, except for few points (see Figure 3e-k, 4a-j and 5a-h). STI can alter the photochemistry of ozone layer in the stratosphere, creating tropospheric westerly winds, which is associated temperature field down to the surface [Kobashi *et al.*, 2013]. Moreover, STI couple with sea-air-land interactions and cloud covers distributions [Lean *et al.*, 2005; Lean, 2010; Rind and Overpeck, 1993; Meehl *et al.*, 2003, 2013]. Many climate models (e.g., Shindell *et al.*, 2001) and other observations (e.g., Koder, 2002; Ineson *et al.*, 2011) report a link between many multi-decadal climate oscillation and variability of STI (e.g., Gray *et al.*, 2010). Moreover,

relation between annual records of STI [*e.g.*, *Lean 2000*] with 30-RM of F/M (i.e., isomer) (0.82), end product of oxocarboxylic, i.e. 30-RM of ω C₂ (0.57), 21-RM of Pyr (0.69) and some what α -dicarbonyls (e.g., Gly) showed positive correlations. It should be noted that oleic acid (C_{18:1}) showed positive correlation with ET (R=0.83) and C₉ (0.74). Similarly, correlation between ω C₉ and C₉ (i.e., oxidation product of C_{18:1} from sea surface slicks) is 0.81 (Table 1). These results suggest that longer chain compounds were oxidized into short chain compounds (e.g., ω C₂ and/or C₉) under strong solar radiation, even we have no other evidences to validate the exact effect of this STI under natural environment at least for Alaskan glaciers.

2.3.7. Response of Ice Core Organic Tracers to Climate Oscillations

There could be other different sources or different factors, which controls the concentration of organic compounds, for example, North Pacific Gyre Oscillation (NPGO) and/or Pacific/North American climate sensitivity index (PNA/PNAI), Arctic Oscillation/North Atlantic Oscillation (AO/NAO) [*Trouet et al., 2009*] and Pacific Decadal Oscillation (PDO) [*MacDonald and Case, 2005*] (see Figure 4k, 4l and 6c). Correlations (R) between 21-RM of total dicarboxylic acids (0.81), oxocarboxylic acid (0.79) and α -dicarbonyls (0.74) with 30-RM of the North Pacific Indices (NPI), which is produced by NCAR's Climate Analysis Section are based on Trenberth and Hurrell [1994] since 1899 to 2008 for November to March (AO and PDO are more active in in these months, e.g., Sun and Wang, 2006, references therein) suggest that deposition and incorporation of these compounds in the Alaskan snow particles could be controlled by intensity of the Aleutian Low (AL) pressure system over the Bering Sea and the Gulf of Alaska. It should be noted that NP indices are the area-weighted sea level pressure (SLP) over the region 30°N-65°N, 160°E-140°W [*Trenberth and Hurrell, 1994*] and NP indices are a good indices for the AL, and it act as the main juncture of the AO-PDO coupling in the NH [*e.g.*, *Sun and Wang, 2006*].

Moreover, ratios of C_2/C_3 and C_2/C_4 (Figure 6a and b) show decadal to multi-decadal historical trends, which are similar to historical trends of PDO (except around 1710s) (Figure 6c) [Mac Donald and Case, 2005]. Correlations (R) between 30-RM of C_2/C_3 and C_2/C_4 with PDO are 0.67 and 0.70, respectively, suggest that oxidizing capacity of the atmosphere (i.e., photochemical ageing) could be altered with the climate periodicity cycle. Hence, historical trends of these ratios (C_2/C_3 , C_2/C_4 and C_3/C_4 ; not shown in figure) and PDO, correlation between diacids and NPI, correlation between diacids and Northern Hemispheric temperature (ET) (e.g., section 3.3.1), and correlation between diacids and STI strongly suggest that organic compounds were likely to be linked with North Pacific index (NPI) and/or PDO and NAO.

Briefly, Brown et al. [2010] clearly showed that the prevailing zonal wind, which comes from Asia to the Pacific regions, can turn from the Gulf of Alaska to Arctic circle-northward by using the wind field at 800, 500 and 200 mb. This zonal wind will be shifted according to PDO and NAO phases (positive and negative). The interaction between PDO [MacDonald and Case, 2005] and NAO [Trouet et al., 2009] phases are very complex (Figure 4l and 6c). We also got lower concentration trends for almost all species after 1860s (except for some points) (Figure 3- 5), which is likely due to positive phase of NAO (Figure 4l). When NAO is positive, there is a strengthening of the Icelandic low-pressure center and Azores high-pressure center, which increase westerly allowing cold air to drain off North America. In contrast, when NAO is negative, there is weakening of both the Icelandic low and Azores high, which drive the jet stream over Alaska and southwest to southeastern part of USA.

This positive phase of NAO could cause restricted/reduced atmospheric transport over Alaskan regions rather than negative phase of NAO. Such type of signal can be observed clearly between historical trends of C_3/C_4 ratios (not shown in figure) and NAO. Similarly, relations between 5-RM of NAO with biogenic tracer (e.g., 5-RM of C_9) and intermediate

compounds between e.g., malic acid (5-RM hC₄) are 0.71 and 0.61, respectively. Some other ice core studies showed that concentrations of chemical compounds and composition are changed due to long term (e.g., El Nino/ENSO) and short-term (e.g., cyclonic activities) climate oscillation in the Northern and Southern Hemisphere [Kaufmann *et al.*, 2010; Legrand and Mayewski, 1997; Kang *et al.*, 2002; Grigholm *et al.*, 2009; Kawamura *et al.*, 1999]. For instance, Tibetan ice core showed the climate proxies and teleconnection with the Pacific Decadal Oscillation (e.g., Grigholm *et al.*, 2009). Kamchatka, Russian ice core (e.g., Sato *et al.*, 2014) clearly showed multi-decadal atmospheric transport from lower latitude to higher latitude in the western Pacific regions, which is associated with PDO and/or NPGO (Figure 7d). It should be noted that contributions of these compounds to WSOC (%) are enhanced significantly (Figure 7a, b and c) since the 1860s with respect to atmospheric transport from lower latitude to higher latitude (e.g., Sato *et al.*, 2014) via photochemical oxidation. Similarly, short chain low molecular weight fatty acids [Kawamura *et al.*, 1996a] and azelaic acid (C₉) of Greenland ice core [Kawamura *et al.*, 1999] showed good agreement with reconstructed Artic temperature departures [Jacoby and D'Arrigo, 1989].

2.4. Conclusions

We found the predominance of oxalic acid followed by adipic and succinic acid. In addition, molecular distribution of ω -oxocarboxylic acids is characterized by the predominance of 9-oxononanoic acid followed by 4-oxobutanic acid and glyoxylic acid. The predominance of 9-oxononanoic acid suggests that most organic species are derived from biogenic unsaturated fatty acids followed by photooxidation. Correlation with climate oscillation indices (e.g., North Pacific index), extra tropical Northern Hemispheric temperature index, solar total irradiance, levoglucosan and dehydroabietic acid suggest that they are produced by the oxidation of precursor compounds emitted from the biogenic and anthropogenic activities. Abrupt change

of concentrations after the 1850s suggests that the transports of organic compounds may have shifted from southeast Alaska. Historical trends of these compounds since the 1980s are controlled by similar meteorological factors, suggesting that the sea-to-air emissions of the organic precursors were associated with lower tropospheric temperature. This study will help to better understand the impact of climate change on oxidizing capability and sources of precursor compounds in perspective with the effect of diacid production variability and its periodic and non-periodic hind cast in the NH.

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Table 1: Correlation coefficients (R^2) among selected dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid and α -dicarbonyls (ng/g-ice) in the ice core from southeast Alaska in 1734 – 2008.

Species	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₉	C ₁₀	Ph	hC ₄	ω C ₂	ω C ₃	ω C ₄	ω C ₉	MeGly
C ₂	1														
C ₃	0.81	1													
C ₄	0.47	0.59	1												
C ₅	0.34	0.42	0.73	1											
C ₆	0.12	0.08	0.18	0.39	1										
C ₇	0.14	0.21	0.43	0.87	0.39	1									
C ₉	0.09	0.06	0.16	0.53	0.59	0.74	1								
C ₁₀	0.08	0.16	-0.04	0.10	0.52	0.22	0.52	1							
Ph	0.13	0.19	0.18	0.26	0.52	0.32	0.36	0.31	1						
hC ₄	0.16	0.22	0.43	0.44	0.17	0.30	0.34	0.07	0.24	1					
ω C ₂	0.57	0.42	0.03	0.18	0.22	0.17	0.28	0.43	0.13	0.11	1				
ω C ₃	0.54	0.55	0.39	0.72	0.32	0.77	0.59	0.32	0.26	0.22	0.55	1			
ω C ₄	0.48	0.54	0.38	0.71	0.34	0.70	0.38	0.16	0.30	0.06	0.33	0.82	1		
ω C ₉	0.05	0.10	0.49	0.79	0.59	0.79	0.67	0.02	0.59	0.49	0.14	0.46	0.38	1	
MeGly	0.52	0.45	0.19	0.23	0.32	0.23	0.38	0.47	0.20	0.24	0.75	0.52	0.22	0.06	1

Table 2: Results of principal component analysis (Varimax rotation with Kaiser Normalization) for concentrations of selected dicarboxylic acids, oxocarboxylic acids, pyruvic acid and α -dicarbonyls (ng/g-ice) in the ice core from southeast Alaska in 1732 - 2009.

Compounds	Components			
	1	2	3	4
Oxalic (C ₂)	0.21	0.74	0.17	0.27
Malonic (C ₃)	0.41	0.68	0.29	0.13
Succinic (C ₄)	0.24	0.82	-0.20	0.06
Glutaric (C ₅)	0.84	0.18	0.08	0.28
Adipic (C ₆)	0.89	0.15	0.21	0.32
Pimelic (C ₇)	0.91	0.17	0.24	0.04
Suberic (C ₈)	0.17	-0.02	0.16	0.89
Azelaic (C ₉)	0.92	0.10	0.26	0.20
Sebacic (C ₁₀)	-0.07	-0.14	0.87	-0.06
Undecanedioic (C ₁₁)	0.12	0.02	0.69	0.23
Methylmalonic (iC ₄)	0.93	0.20	0.21	-0.03
2-Methylglutaric (iC ₆)	0.93	0.11	0.05	0.18
Maleic (M)	0.05	0.61	-0.03	0.03
Fumaric (F)	0.44	0.08	0.32	0.19
Methylmaleic (mM)	0.86	0.29	0.22	0.24
Phthalic (Ph)	0.42	0.24	0.46	0.64
Oxomalonic (kC ₃)	0.29	0.72	0.30	0.04
4-Oxopimelic (kC ₇)	0.96	0.13	-0.05	-0.13
Glyoxylic (ω C ₂)	0.35	0.13	0.73	0.12
3-Oxopropanoic (ω C ₃)	0.73	0.30	0.34	0.38
4-Oxobutanoic (ω C ₄)	0.75	0.23	0.42	0.27
5-Oxopentanoic (ω C ₅)	0.92	0.14	0.16	0.29
7-Oxoheptanoic (ω C ₇)	0.97	0.12	0.01	0.03
8-Oxoctanoic (ω C ₈)	0.94	0.19	-0.05	0.13
9-Oxononanoic (ω C ₉)	0.53	0.28	-0.14	0.62
Glyoxal (Gly)	0.93	0.15	0.13	0.21
Methylglyoxal (mGly)	0.66	0.28	0.23	0.19

Table 3. Concentrations of dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid and α -dicarbonyls in ice core samples from southeast Alaska in 1665 - 2008, and intervals of 1665-1860, 1861-1979 and 1980-2008.

		Concentrations (ng/g-ice)					
Compounds	Chemical formula	1665-2008			1665-1860	1861-1979	1980-2008
		Range	Mean	SD	Mean		
Oxalic (C ₂)	HOOC-COOH	2.01-27.8	7.17	4.18	7.92	6.42	7.03
Malonic(C ₃)	HOOC-CH ₂ -COOH	0.01-2.95	0.76	0.53	0.95	0.59	0.69
Succinic(C ₄)	HOOC-(CH ₂) ₂ -COOH	0.36-16.2	4.3	3.2	6.59	3.56	1.96
Glutaric (C ₅)	HOOC-(CH ₂) ₃ -COOH	0.10-19.2	2.19	3.43	3.40	1.06	1.82
Adipic (C ₆)	HOOC-(CH ₂) ₄ -COOH	BDL-60.1	4.99	10.5	7.60	0.83	6.41
Pimelic (C ₇)	HOOC-(CH ₂) ₅ -COOH	0.02-7.70	0.67	1.28	1.02	0.15	0.80
Suberic (C ₈)	HOOC-(CH ₂) ₆ -COOH	0.05-9.93	1.65	2.29	1.84	0.32	3.01
Azelaic (C ₉)	HOOC-(CH ₂) ₇ -COOH	0.16-11.8	2.65	2.95	3.03	1.11	4.01
Sebacic (C ₁₀)	HOOC-(CH ₂) ₈ -COOH	BDL-5.73	0.65	1.19	0.55	0.31	1.22
Undecanedioic (C ₁₁)	HOOC-(CH ₂) ₉ -COOH	BDL-7.70	0.85	1.68	0.82	0.43	1.42
Methylmalonic (iC ₄)	HOOC-CH(CH ₃)-COOH	0.02-9.44	0.77	1.48	1.23	0.23	0.79
Methylsuccinic (iC ₅)	HOOC-CH(CH ₃)-CH ₂ -COOH	BDL-3.47	0.34	0.45	0.51	0.29	0.16
2-Methylglutaric (iC ₆)	HOOC-CH(CH ₃)-(CH ₂) ₂ -COOH	0.02-3.21	0.27	0.51	0.41	0.09	0.28
Maleic (M)	HOOC-CH = CH-COOH	0.01-1.74	0.15	0.23	0.22	0.06	0.17
Fumaric (F)	HOOC-CH = CH-COOH	BDL-2.52	0.32	0.52	0.32	0.07	0.56
Methylmaleic (mM)	HOOC-C(CH ₃) = CH-COOH	BDL-2.65	0.3	0.42	0.45	0.09	0.34
Phthalic (Ph)	HOOC-(C ₆ H ₄)-COOH	BDL-27.7	3.24	5.21	3.63	0.91	5.55
Malic (hC ₄)	HOOC-CH(OH)-CH ₂ -COOH	BDL-5.96	0.63	1.24	0.49	0.15	1.28
Oxomalonic (kC ₃)	HOOC-C(O)-COOH	0.03-0.77	0.18	0.16	0.21	0.12	0.22
4-Oxopimelic (kC ₇)	HOOC-(CH ₂) ₂ -C(O)-(CH ₂) ₂ -COOH	0.01-2.34	0.24	0.41	0.42	0.08	0.18
Total annual average dicarboxylic acids		4.35-180	32.2	34.8	41.5	16.8	37.8
Glyoxylic (ω C ₂)	OHC-COOH	0.03-4.72	0.93	1.05	0.90	0.32	1.61
3-Oxopropanoic (ω C ₃)	OHC-CH ₂ -COOH	0.01-4.12	0.4	0.59	0.59	0.14	0.45
4-Oxobutanoic (ω C ₄)	OHC-(CH ₂) ₂ -COOH	0.01-4.68	0.99	1.12	1.09	0.35	1.63
5-Oxopentanoic (ω C ₅)	OHC-(CH ₂) ₃ -COOH	BDL-5.36	0.8	1.21	1.06	0.14	1.26
7-Oxoheptanoic (ω C ₇)	OHC-(CH ₂) ₅ -COOH	BDL-5.33	0.64	1.01	0.79	0.11	1.06
8-Oxooctanoic (ω C ₈)	OHC-(CH ₂) ₆ -COOH	BDL-4.04	0.46	0.56	0.60	0.21	0.55
9-Oxononanoic (ω C ₉)	OHC-(CH ₂) ₇ -COOH	0.01-5.41	1.13	1.22	1.64	0.59	1.11
Total annual average ω-oxocarboxylic acids		0.47-26.5	5.31	5.52	6.65	1.85	7.70
Pyruvic(Pyr)	CH ₃ -C(O)-COOH	0.01-5.60	1.43	0.97	1.37	1.37	1.59
Glyoxal (Gly)	OHC-CHO	BDL-1.52	0.28	0.32	0.29	0.13	0.45
Methylglyoxal (MeGly)	CH ₃ -C(O)-CHO	0.01-2.80	0.39	0.50	0.50	0.15	0.53
Total annual average α-dicarbonyls		0.08-3.29	0.67	0.68	0.80	0.28	0.98

DL=Below detection limit (0.001 ng/gm-ice)

Figure Captions

Figure 1. Map showing the geographical region of Aurora peak of Alaska, where 180-meter long ice core sample was drilled on saddle of this peak in 2008.

Figure 2. Average molecular distributions of diacids, oxoacids, pyruvic acid and dicarbonyls in the ice core records since 1665 - 2008 collected from Aurora peak of Alaska and error bar represents the standard deviation of individual species.

Figure 3. Concentration changes of (a) total dicarboxylic acids, (b) – (k) individual dicarboxylic acids (C_2 - C_{11}) in the Alaskan ice core collected from Aurora Peak and (l) ice core depth v.s. year [Tsushima *et al.*, 2014]. All species showed the statistically (t-test) significant ($p = 0.000$).

Figure 4. Concentration changes of (a) - (c) branched chain saturated dicarboxylic acids (iC_4 , iC_5 and iC_6), (d) – (g) unsaturated dicarboxylic acids (M, F, mM and Ph) and (h) –(j) multifunctional diacids (hC_4 , kC_3 and kC_7) in the Alaskan ice core collected from saddle of Aurora Peak. Similarly, (k) North Pacific index (NPI) since 1898-2008 based on Trenberth and Hurrell [1994], (l) multi-decadal North Atlantic oscillation (NAO) reconstruction since 1730 - 1995 [Trouet *et al.*, 2009] (m) reconstructed solar total irradiance (STI) since 1660- 2000 [Lean, 2000], . All species showed the statistically (t-test) significant ($p = 0.000$), except for phthalic (Ph). Concentration of phthalic (Ph) is also statistically significant ($p = 0.000$) except for the highest point (27.7 ng/g-ice) in 1840 ($p = 0.178$).

Figure 5. Concentration changes of total ketocarboxylic acids, ketoacids (ωC_2 - ωC_9),

pyruvic acid (Pyr), total dicarbonyls and dicarbonyls (Gly and MeGly) in the Alaska ice core records collected from saddle of Aurora peak. All species showed the statistically (t-test) significant ($p = 0.000$).

Figure 6. Concentration ratios of (a) C_2/C_3 , (b) C_2/C_4 and (c) 11 years running mean (11-RM) of reconstructed Pacific decadal oscillation (PDO) index since 1660 - 1996 [MacDonal and Case, 2005]. Similarly, (d) 5 years running mean (5-RM) of reconstruction of extra tropical Northern Hemisphere annual temperature departure (ET) observed in the instrumental record since 1750-2000 [Wilson et al., 2007].

Figure 7. Historical variations of contributions of compound classes to WSOC (%) (a) total diacids (b) total oxoacids (c) total α -dicarbonyls in the Alaskan ice core from 1665 to 2008 and (f) 20-year running mean of hydrogen isotope ratios (δD) in ice core from Kamchatka Peninsula, Russia (Sato et al., 2014).

Figure 8a. Comparison of three decades changes in the concentrations of average (a) dicarboxylic acids, (b) oxocarboxylic acids (c) α -dicarbonyls and (d) pyruvic acid since Jan 1979 – 2008.

Figure 8b. NOAA'S TIROS-N weather satellites lower tropospheric temperature anomaly since 1979 – 2008. (source: http://science1.nasa.gov/science-news/science-at-nasa/1997/essd12mar97_1/).

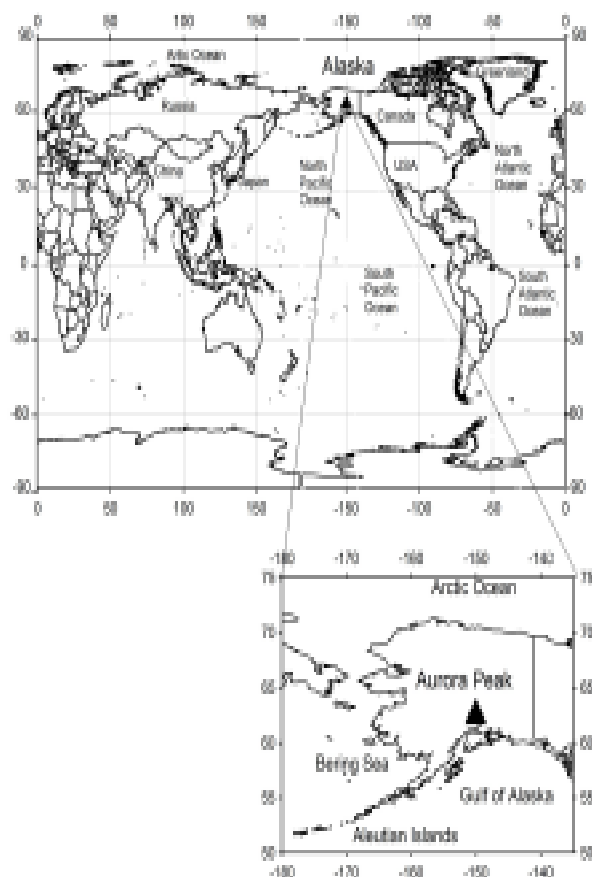


Figure 1. Map showing the geographical location of Aurora Peak of Alaska, from which 180-meter long ice core sample was drilled on the saddle of this peak in 2008.

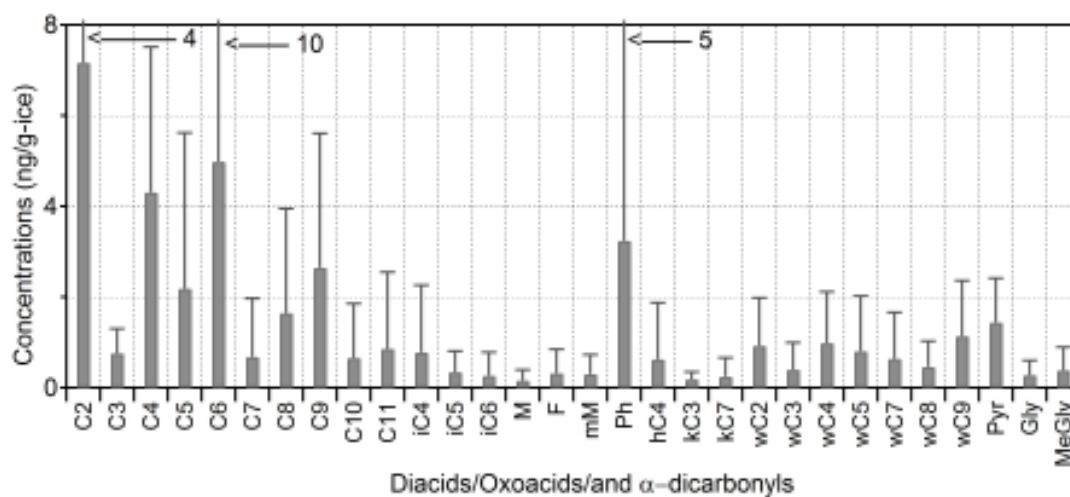


Figure 2. Average molecular distributions of diacids, oxoacids, pyruvic acid and α -dicarbonyls in the ice core collected from Aurora Peak of Alaska since 1665 – 2008 and error bar represents the standard deviation of individual species.

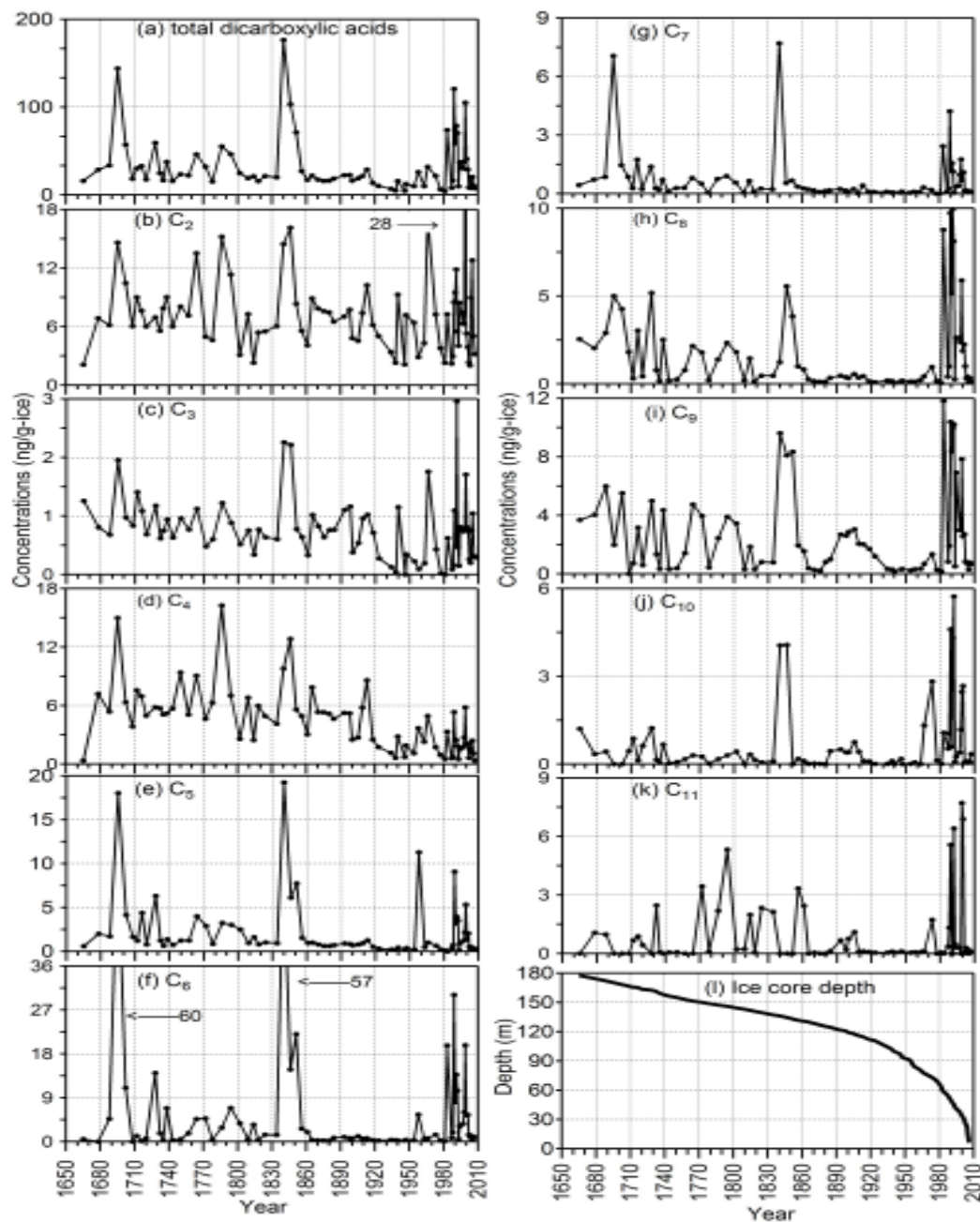


Figure 3. Concentration changes of (a) total dicarboxylic acids, (b) – (k) individual dicarboxylic acids (C₂ - C₁₁) in the Alaskan ice core collected from Aurora Peak and (l) ice core depth v.s. year [Tsushima *et al.*, 2014]. All species showed the statistically (t-test) significant ($p = 0.000$).

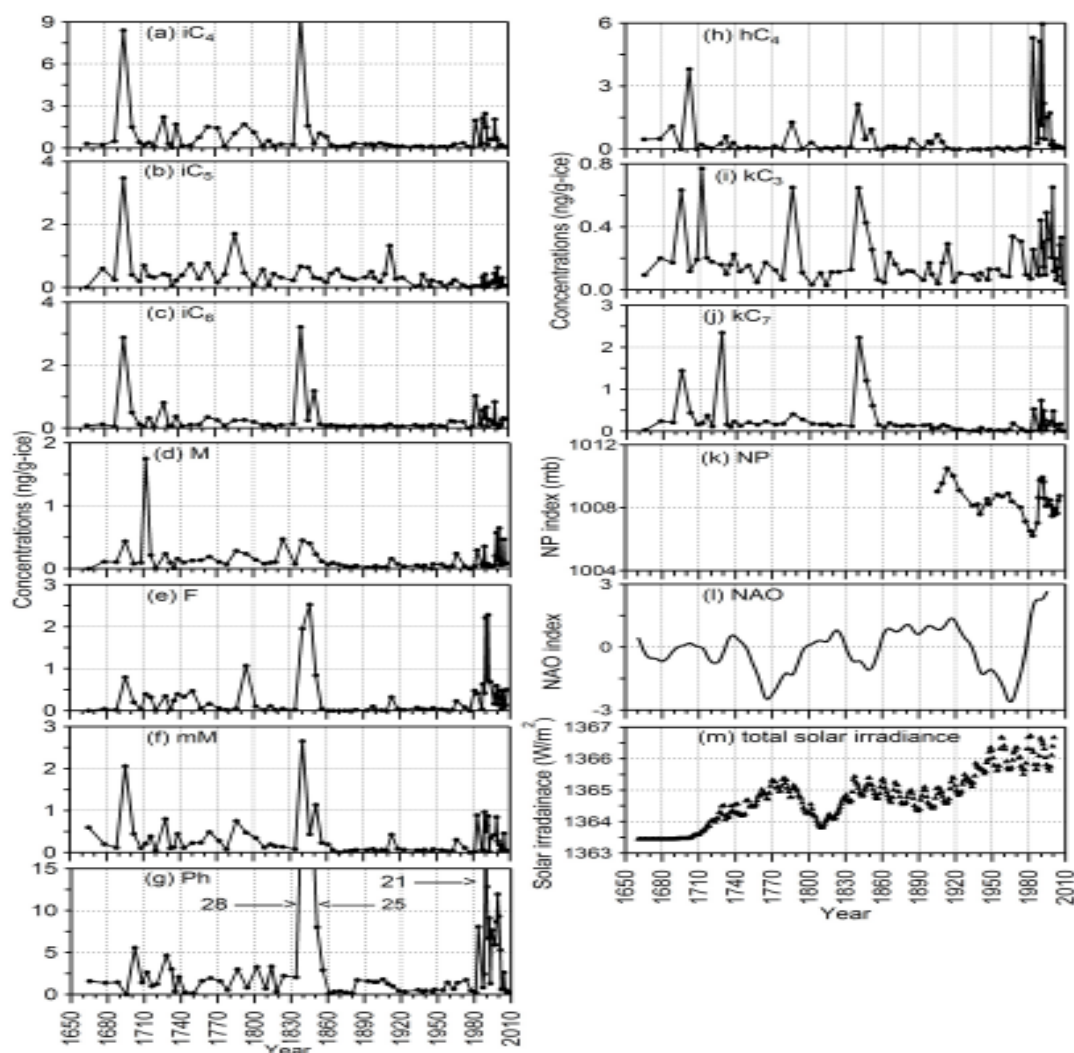


Figure 4. Concentration changes of (a) - (c) branched chain saturated dicarboxylic acids (iC_4 , iC_5 and iC_6), (d) – (g) unsaturated dicarboxylic acids (M, F, mM and Ph) and (h) –(j) multifunctional diacids (hC_4 , kC_3 and kC_7) in the Alaskan ice core collected from saddle of Aurora Peak. Similarly, (k) North Pacific index since 1898-2008 based on *Trenberth and Hurrell [1994]*, (l) multi-decadal North Atlantic oscillation reconstruction (NAO) since 1730 - 1995 [*Trouet et al., 2009*] (m) reconstructed solar total irradiance since 1660- 2000 [*Lean, 2000*], . All species showed the statistically (t-test) significant ($p = 0.000$), except for phthalic (Ph). Concentration of phthalic (Ph) is also statistically significant ($p = 0.000$) except for the highest point (27.7 ng/g-ice) in 1840 ($p = 0.178$).

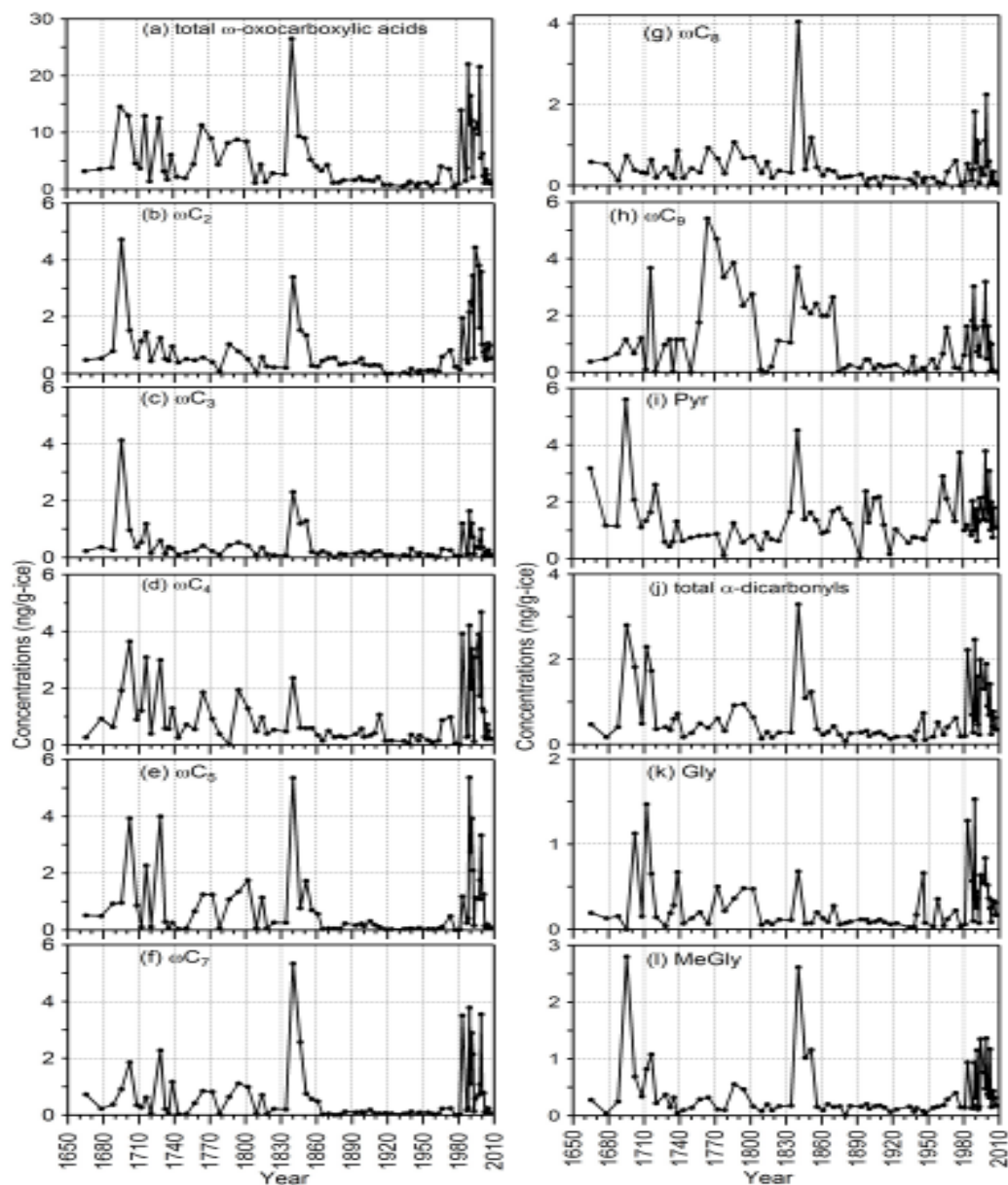


Figure 5. Concentration changes of (a) total oxocarboxylic acids, (b) – (h) individual oxoacids (ω C₂ - ω C₉), (i) pyruvic acid (Pyr), (i) total α -dicarbonyls, (k) glyoxal (Gly) and (l) methylglyoxal (MeGly) in the Alaskan ice core collected from the saddle of Aurora Peak. All species showed the statistically (t-test) significant ($p = 0.000$).

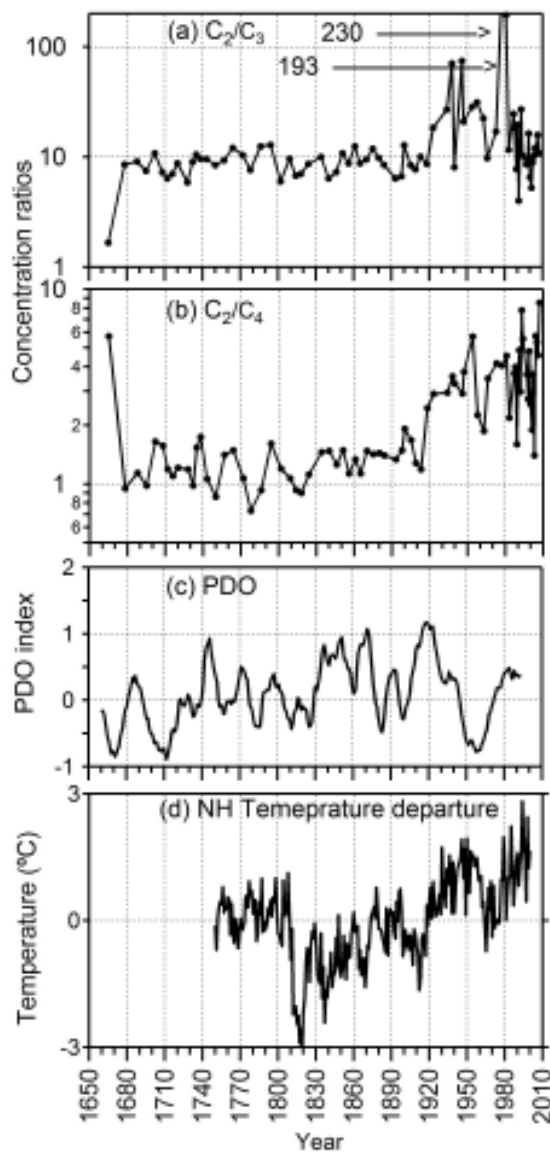


Figure 6. Concentration ratios of (a) C_2/C_3 , (b) C_2/C_4 and (c) 11 years running mean (11-RM) of reconstructed PDO index since 1660 - 1996 [MacDonal and Case, 2005]. Similarly, (d) 5 years running mean (5-RM) of reconstruction of extra tropical Northern Hemisphere annual temperature departure (ET) observed in the instrumental record since 1750-2000 [Wilson *et al.*, 2007].

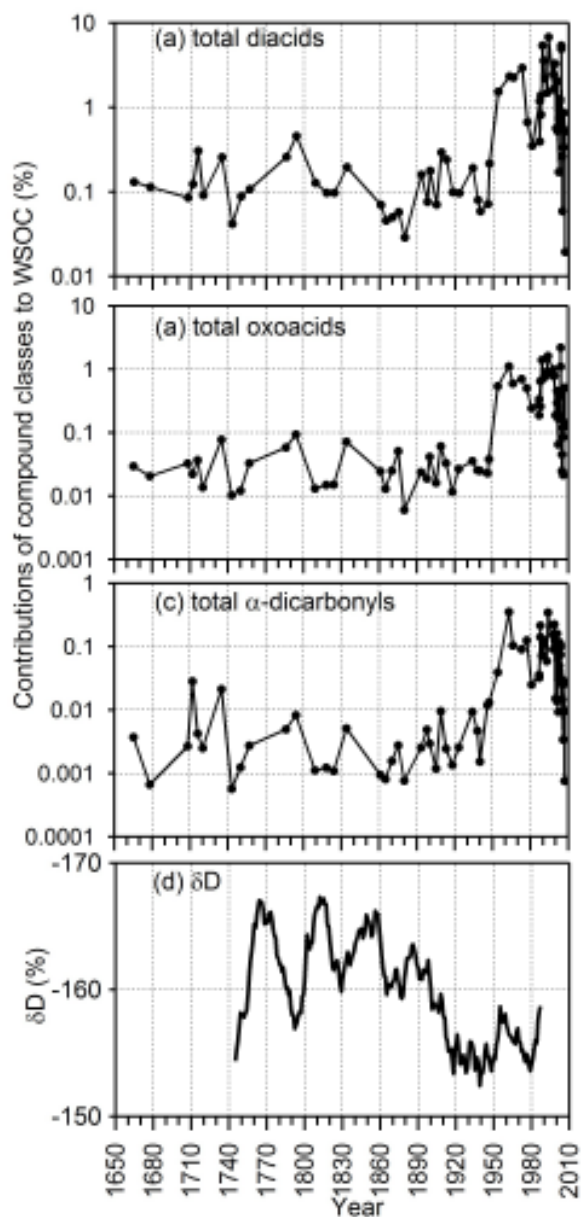


Figure 7. Historical variations of contributions of compound classes to WSOC (%) (a) total diacids (b) total oxoacids (c) total α -dicarbonyls in the Alaskan ice core from 1665 to 2008 and (d) 20-year running mean of hydrogen isotope ratios (δD) in ice core from Kamchatka Peninsula, Russia [Sato *et al.*, 2014].

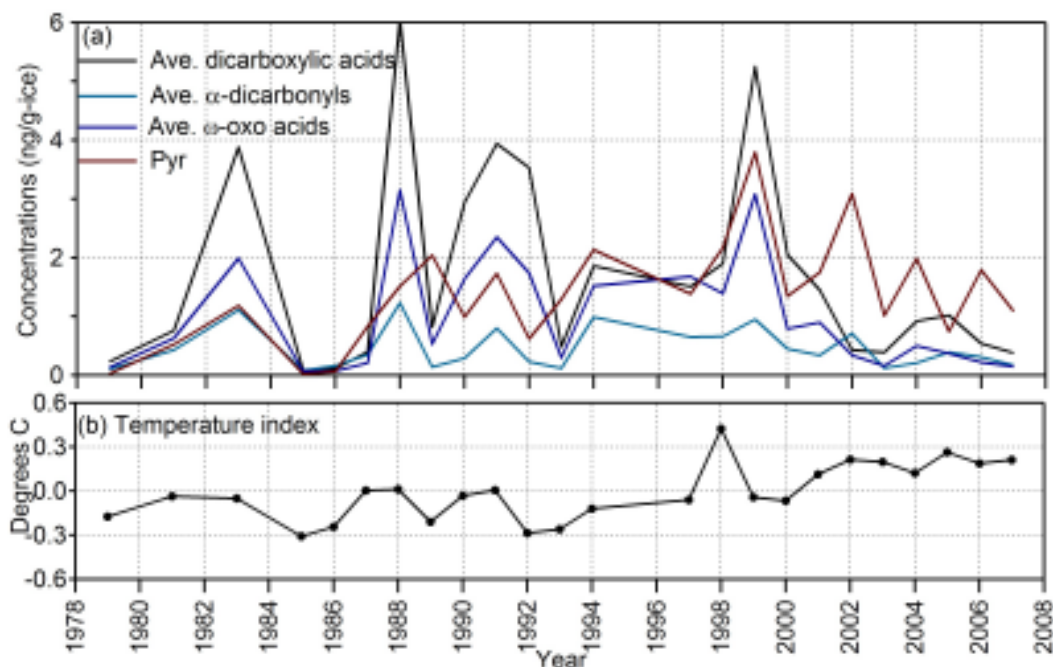


Figure 8a. Comparison of three decades changes in the concentrations of average (a) dicarboxylic acids, (b) oxocarboxylic acids (c) α -dicarbonyls and (d) pyruvic acid (Pyr) since Jan 1979 – 2008. Similarly, Figure 8b shows the three decades changes in the NOAA'S TIROS-N weather satellites global lower tropospheric temperature anomalies (Jan 1979 – May 2008, source: http://science1.nasa.gov/science-news/science-at-nasa/1997/essd12mar97_1/).

Chapter 3: Ice core profiles of saturated fatty acids (C_{12:0} - C_{30:0}) and oleic acid (C_{18:1}) from southern Alaska since 1665 AD: A link to climate change in the Northern Hemisphere

3.1. Introduction

Alkyl lipids such as *n*-fatty acids as well as *n*-alkanes and *n*-alkanols that are ubiquitous in continental (*Simoneit et al., 1991; Simoneit and Mazurek, 1982; Ho et al., 2011*) and remote marine aerosols (*Conte and Weber, 2002; Kawamura et al., 2003; Bendle et al., 2007; Mochida et al., 2007*). They are emitted from biogenic sources including terrestrial higher plants, soil organic matter, microbial activities and marine phytoplankton (*Kawamura et al., 1996; Rogge et al., 1993, 2006; Seki et al., 2010*). Hence, alkyl lipids can be used as organic tracers to investigate the sources of organic aerosols and long-range atmospheric transport (*Kawamura et al., 1995; Fang et al., 2002*).

Fatty acids can be deposited over ice sheet and be stored in ice for several hundred years or more (*Kawamura et al., 1995, 1996; Nishikiori et al., 1997*). Fatty acids are produced by biological activities of many biota (*Fang et al., 2002*). For example, oleic acid (C_{18:1}) is the major constituent of cell membranes in marine phytoplankton and terrestrial higher plants and can be emitted to the atmosphere directly from the leaf surface and wood combustion as well as bubble bursting in the surface ocean (*Kawamura and Gagosian, 1987; Marty et al., 1979; Fine et al., 2001*). However, there are very few studies on the homologous series of fatty acids (C_{12:0} - C_{30:0}) in ice core samples from Greenland and Antarctica ice sheets (*Kawamura et al., 1996; Nishikiori et al., 1997*). In particular, ice core collected from mountain glacier has not been explored for fatty acids yet.

Fatty acids in ice core are closely related to past climatic changes (*Kawamura et al., 1995, 1996; Nishikiori et al., 1997*). Their ice core profiles can be employed as a proxy to assess the past changes in marine and terrestrial emissions on multi-decadal-to-centennial time scales. Here, we investigated homologous series of straight chain fatty acids (C_{12} - C_{30}) from Aurora Peak of Alaska to better understand the past atmospheric transport of fatty acids and to reconstruct the paleoclimate conditions and sources of fatty acids since 1665 – 2008. The historical trends of fatty acids are discussed in terms of past changes in atmospheric circulation in the northern North Pacific and its surroundings.

3.2. Ice Core Samples and Analytical Procedures

Aurora Peak of Alaska (APA) is located in the southeast of Fairbanks (63.521°N , 146.542°W) with an elevation of 2,825 meter above sea level (see chapter 2, Figure 1). Fatty acids were determined using butyl ester derivatization method (*Mochida et al., 2003*). Numbers of total ice core sections are 122, which is equivalent to ~35% of the 180 m long ice core recovered from the APS site.

100 mL of melt water from ice core section were placed into a pear shape flask (300 mL) and the pH of the sample was adjusted to 8.5-9.0 using a 0.05 M KOH solution. The samples were concentrated down to near 5 mL using a rotary evaporator under vacuum. The concentrates were transferred to a pear shape flask (50 mL), concentrated until dryness using a rotary evaporator under vacuum, and then reacted with ~0.25 mL of 14% boron trifluoride (BF_3)/n-butanol to derive carboxyl groups to butyl esters at 100°C for 1 hour. The butyl ester derivatives were determined using a capillary gas chromatography (GC; HP 6890). The GC peak identification was performed using a GC/MS (Agilent). The laboratory blanks of $C_{14:0}$, $C_{16:0}$, $C_{17:0}$, $C_{18:0}$,

$C_{18:1}$, $C_{20:0}$, $C_{22:0}$ and $C_{24:0}$ relative to real samples were 3.9, 3.7, 1.8, 4.1, 3.8, 2.6, 1.7 and 2.4 %, respectively. The analytical errors for $C_{14:0}$, $C_{16:0}$, $C_{17:0}$, $C_{18:1}$, $C_{20:0}$, $C_{24:0}$ and $C_{28:0}$ fatty acids in the replicate analyses were 4.9, 3.1, 9.3, 3.5, 1.6, 2.6 and 2.5%, respectively. Here, we present concentrations of lower molecular weight fatty acids ($C_{12:0}$ - $C_{19:0}$: LFAs) and higher molecular weight fatty acids ($C_{20:0}$ - $C_{30:0}$: HFAs), which are all corrected for procedural blanks.

Yasunari and Yamazaki, (2009) reported 10-day backward trajectory based on Lagrangian tracking method for 1992 - 2002 and suggested that southeast Alaskan regions can receive more air masses from the adjacent areas of the northern North Pacific regions, East Asia, Eastern Russia-Siberia, the Okhotsk-Bering Seas, higher latitudes of Alaskan regions, Japan, Canada and the Arctic Ocean in the troposphere (>300 hPa). Moreover, Cahill (2003) suggested that chemical compositions of Alaskan aerosols are dominated by oceanic components.

3.3. Results

Figure 2 shows the average molecular distribution of homologous series of straight chain fatty acids ($C_{12:0}$ - $C_{30:0}$) including unsaturated fatty acid (oleic acid, $C_{18:1}$) for 1665 - 2008. Their molecular distributions are characterized by a strong even carbon number predominance with a peak at $C_{16:0}$. $C_{16:0}$ comprised one third (av. 30.6%) of total fatty acids, followed by $C_{14:0}$ (19.3%) and $C_{18:1}$ (14.4%). The concentrations of $C_{16:0}$, $C_{18:1}$ and $C_{14:0}$ range from below detection limit (BDL: 0.001ng/g-ice) to 95.1 ng/g (av. $20.3 \pm SD 29.8$ ng/g-ice), BDL to 189 ng/g (19.6 ± 38.6 ng/g-ice), BDL to 91.3 ng/g (15.3 ± 21.9 ng/g-ice), respectively. We also detected significant amounts of $C_{18:0}$ and $C_{12:0}$ (Table 1). HFAs ($C_{20:0}$ - $C_{30:0}$) are dominated by lignoceric acid ($C_{24:0}$), followed by arachidic ($C_{20:0}$) and behenic ($C_{22:0}$)

acid (Figure 2 and Table 1).

Figure 3 shows historical changes of selected LFAs in the ice core collected from Aurora Peak in Alaska. Palmitic acid ($C_{16:0}$), which is the most abundant FA species, showed several peaks around the years of 1738, 1780, 1840, 1990 and 2000. Interestingly, all the components of LFAs showed a large spike around 1840-1860 (Figure 3). The historical trend of $C_{12:0}$ is similar to that of $C_{15:0}$, except for few points. The trends of $C_{12:0}$ and $C_{15:0}$ are different than those of other LFA components, except for some points. For instance, around 1850s and after 1980s similar types of higher spikes were observed (Figure 3a-3g). Figure 4 presents concentration changes of selected HFAs ($C_{20:0}$ - $C_{26:0}$) in the ice core. Although HFAs showed large spikes around at 1690s and 1840s, their historical trends are not always similar to those of LFAs. Concentrations of HFAs are relatively low during the period from 1860s to 1970s (Figures 3 and 4). Except for few points, HFA species showed similar historical trends each other with peaks at around 1690s, 1840s and 1980s (Figure 4a – 4f).

3.4. Discussion

3.4.1. Molecular compositions of fatty acids and their historical profile

The homologous series of fatty acids show a strong even carbon number predominance with a peak at $C_{16:0}$ followed by $C_{18:1}$ and $C_{14:0}$ as described above. The predominance of $C_{16:0}$ has also been reported in riverine and estuarine sediments (Naraoka and Ishiwatari, 2000), marine sediments (Ohkouchi *et al.*, 1997), soil samples (Matsumoto *et al.*, 2007) and remote marine aerosols (Conte and Weber, 2002; Bendle *et al.*, 2007). LFAs are mainly originated from marine phytoplankton (Kawamura and Gagosian, 1987; Kawamura, 1995; Marty *et al.*, 1979), while HFAs

are originated from terrestrial higher plants and soil dust (*Kawamura et al., 1996; Ohkouchi et al., 1997*). The molecular distributions of fatty acids in this study are different than those from other studies on aerosols (*Kawamura et al., 2010; Fang et al., 2002*) and ice cores from Antarctica (*Nishikiori et al., 1997*) and Greenland site-J (*Kawamura et al., 1995, 1996*). For example, fatty acids in Greenland site-J ice core are characterized by a strong even carbon number predominance with maximum at C₁₆ or C₂₂ followed by C₂₄ and lesser abundance of C_{18:1} (*Kawamura et al., 1995, 1996*).

Unsaturated LFAs such as C_{18:1} are abundant in marine phytoplankton (especially diatom) (*Napolitano et al., 1997*) and are dominant in the sea surface micro layer (*Marty et al., 1979; Garret, 1967*). Hence, the higher abundance of C_{18:1} than C_{18:0} in our ice core suggests an enhanced emission of C_{18:1} from the surrounding oceans via long-range atmospheric transport to Alaskan ice core site. This is consistent with the fact that diatom is dominant species in high latitudinal oceans (*Napolitano et al., 1997*) and C_{18:1} is one of a dominant marine fatty acid in the sea surface micro layer (*Kawamura and Gagosian, 1987; Marty et al., 1979*). In general, unsaturated FAs are labile compounds compared to saturated ones and can be easily decomposed during long-range transport (*Kawamura and Gagosian, 1987*). However, C_{18:1} was abundantly detected in almost all ice core sections, suggesting that the deposition and subsequent incorporation of fresh marine aerosol components in the glacier occurred without severe photochemical degradation during atmospheric transport. This suggests that APA is an excellent site to record the historical changes in emission and transport of fresh marine organic matter from the surrounding oceans.

LFAs (except for C_{12:0} and C_{15:0}) showed similar historical profiles each other (Figure 3a – 3g) with lower concentration after 1860s to 1980s, suggesting a marked

decrease in the sea-to-air emission and subsequent transport of FAs during the period. In contrast, total FA concentrations gradually increased after 1960s, except for few points around 1875, 1923, 1977 and 2005 (Figure 5a). The lower concentrations of LFAs during 1860-1980 AD (Figure 5c) may be in part attributed to depressed emission of marine derived fatty acids probably due to the extension of sea ice coverage around the Alaskan regions. In fact, sea ice reconstruction in Arctic region including the Chukchi Sea shows a significant expansion of sea ice area during the period (*de Vernal et al., 2008; Kinnard et al., 2011; Cavalieri et al., 1997*). Another reason for the decreased concentrations of LFAs may be the shifting of atmospheric transport over Aurora Peak in Alaska, which could be associated with multi-decadal climatic cycle in the Pacific regions (Figure 5d and 5f), a point to be discussed later. We have presented a vertical depth profile of ice core as a function of the proposed chronology by Tsushima et al. (2014) (Figure 5g).

In contrast, the high concentrations of LFAs before 1860s may be in part associated with an enhanced phytoplankton productivity in the open ocean due to the retreat of sea ice and an enhanced emission of fatty acids via bubble bursting processes from sea surface micro layers (*de Vernal et al., 2008; Kinnard et al., 2011; Kawamura and Gagosian, 1987; Garrett, 1976*). In fact, high concentrations of fatty acids like $C_{14:0}$, $C_{16:4\omega1}$ and $C_{20:5\omega3}$ have been reported during the phytoplankton bloom whereas $C_{18:0}$, $C_{18:1\omega9}$, $C_{18:2\omega2}$ and $C_{18:4\omega3}$ were abundantly detected during the post bloom of phytoplankton in the east coast of Canada (*Napolitano et al., 1997*). Moreover, there could be some other contributors, for instance, from bacteria, spores, pollen, plant organelles, leaf cells, chloroplast and microbial lipids by soil remobilization (*Rogge et al., 1993; Simoneit, 1989; Kawamura et al., 2003; 2010*) as well as biomass burning (Oros and Simoneit, 1999). Interestingly, Nishikiori et al.

(1997) reported higher concentrations of fatty acids in the Site H15 of Antarctica after 1850s and considered the results due to the enhanced sea-to-air emission of marine-derived fatty acids. Higher spikes of fatty acids could be caused by the retreat of sea ice and subsequent expansion of open ocean water associated with global warming (*de Vernal et al., 2008; Kinnard et al., 2011; Kawamura et al., 1995, 1996; Nishikiori et al., 1997*).

Detection of HFAs are characterized in the ice core suggests that the deposition of terrestrial plant-derived HFAs occurred over the saddle of APA. HFAs are originated from epicuticular waxes of terrestrial higher plants and soil dust (*Simoneit and Mazurek, 1982; Ho et al., 2010, 2011*). It should be noted that we confirmed by visible observation the presence of soil dust particles in few ice core sections in this study. Cahill (2003) reported, based on the chemical composition study of Alaskan aerosols that Europe, Russia, Asia and other upwind areas are significant source regions for the aerosol loading over and/or around the North Pacific regions. In addition, higher plant-derived pollens, fungi, bacteria, spores and soil organic matter can easily supply HFAs in the atmosphere with high-speed winds (*Lechevalier, 1977*). Updraft of wind from earth surface to cloud level and/or any type of atmospheric instability could act as a driving force for the significant transport of HFAs over the ice sheet at high mountains.

The concentration ratios of atmospheric compounds can be used to determine the origin of these atmospheric tracers and sometimes source, sinks and other important hidden characteristics. Alkanoic acids $<C_{20}$ can be derived from marine phytoplankton, bacteria, spores, and organic detritus as mentioned above. Thus, ratio of $\geq C_{22}/<C_{20}$ under 1 and C_{max} at C_{16} and C_{18} can reflect microbial activities for aerosols with less contribution from terrestrial higher plants (*Fang et al., 1999*;

Oliveira et al., 2007). Interestingly, the ratio obtained in this study is 0.13, which is significantly lower than 1.0 with $C_{\max}$ at C_{16} . This again suggests that fatty acids in the ice core are mainly derived from marine biota via sea-to-air emission and subsequent atmospheric transport over the Alaskan mountain area.

Once unsaturated fatty acids (indicators of recent biogenesis) are emitted to the atmosphere from the ocean surface, the double bond in their structures can be oxidized by OH radicals, ozone and other oxidants, resulting in aldehydes and dicarboxylic acids (*Kawamura and Gagosian, 1987; Kawamura et al., 1995*). Thus, the concentration ratios between saturated alkanolic acid ($C_{18:0}$) and unsaturated alkenoid acid ($C_{18:1}$) can be used as a proxy to estimate the atmospheric aging of organic aerosols. For instance, Ho et al. (2010) used such ratios to discuss the photochemical aging of organic aerosols. We found higher $C_{18:1}/C_{18:0}$ ratios around at 1730s, 1850s, 1950s and after 1980s (Figure 5e), suggesting that marine-derived fresh organic aerosols were more frequently transported and stored in the ice core without severe photochemical processing in the air and on the glacier. On the other hand, lower $C_{18:1}/C_{18:0}$ ratios were recorded during 1660s-1710s, 1750s, 1810s, 1870s and 1920s (Figure 5e), suggesting that oleic acid was more oxidized during the long distance transport before the wet scavenging over the saddle of APA.

3.4.2. Multiple Responses of Alaskan Ice Core to Climate Change

We found a strong correlation between photochemical tracer; azelaic acid (C_9) (Pokhrel et al., unpublished result) and $C_{18:1}$ ($R=0.83$), $C_{18:0}$ (0.75), and total LFAs ($C_{12:0} - C_{19:0}$) (0.83). Because azelaic acid is a photo-oxidation product of unsaturated fatty acids (*Kawamura and Gagosian, 1987*), the positive correlations suggest that the sea-to-air emission is the major source of LFAs in ice core and variations of

photochemical degradation was not significant during the period. However, as seen in Figure 5e, a significant variation of $C_{18:1}/C_{18:0}$ ratios was detected in the ice core profile, a point to be discussed later. In contrast, levoglucosan is a unique biomass-burning tracer (*Simoneit, 2002*) did not show the spikes in 1850s when LFAs are abundant in the ice core (Figure 5c). However, almost all compounds (diacids and fatty acids) showed higher spikes in 1850s (Figures 3, 4 and 5). No correlation of levoglucosan with palmitic acid ($C_{16:0}$) ($R = 0.10$), $C_{18:0}$ (0.07), $C_{18:1}$ (0.11) and LFAs ($C_{12:0} - C_{19:0}$) (0.33) suggest that biomass burning is not a major source of fatty acids in ice core.

We detected significant amounts of sugar compounds including arabitol, mannitol, inositol (sources: virus, bacteria, algae and fungal spores), α -glucose, β -glucose, α -fructose, β -fructose (pollen, fruits and yeast fragments), trehalose (fungi, bacteria, soil surface and unpaved dust) and sucrose (buds and roots) (*Fu et al., 2012, and references therein*) in the ice core for the years of 1734 – 2008 (Pokhrel et al., unpublished results). However, we found very weak or no correlations ($R < 0.14$) between LFAs ($C_{12:0} - C_{19:0}$) and the above mentioned sugar compounds, indicating that the terrestrial sources are not main contributors of ice core LFAs. This again suggests that marine sources are important sources of LFAs in ice core.

LFAs showed weak or no correlation with some inorganic ions (unpublished results). For example, correlation coefficients (R) of $C_{18:1}$ with $nss-K^+$, $nss-Ca^+$ and NH_4^+ are 0.11, 0.23 and 0.02, respectively. $nss-K^+$ is a good tracer of biomass burning (*Simoneit, 1989*) whereas Ca^+ is abundant in continental dusts (*Kawamura et al., 2004; Mkombe and Kawamura, 2014; Kunwar and Kawamura, 2014*). Similarly, very weak correlations (<0.19) were found for fatty acids ($C_{14:0}$, $C_{16:0}$, $C_{17:0}$, and $C_{18:0}$) with NO_2^- or NO_3^- , which are abundant in continental polluted aerosols (*Legrand and*

Mayewski, 1997, references therein). These results suggest that LFAs are not derived from continental sources.

In contrast, we found a positive correlation between Na^+ and $\text{C}_{18:1}$ ($R = 0.67$), and Na^+ and LFAs ($R=0.50$). The slightly weaker correlation may be due to the possible fractionation between Na^+ and LFAs during the bubble bursting process in the ocean surface. We also found a positive correlation between methanesulfonate (MSA^-) (a good tracer of marine biological activity: oxidation product of dimethyl sulfide (DMS) emitted from the ocean by microbial activity, e.g., Miyazaki et al. (2010), and $\text{C}_{16:0}$ ($R=0.81$), $\text{C}_{18:0}$ (0.77) and $\text{C}_{18:1}$ (0.49). Relatively low value for $\text{C}_{18:1}$ may be caused by its photochemical oxidation during atmospheric transport. On the other hand, correlation coefficients for $\text{C}_{16:0}$, $\text{C}_{18:0}$ and $\text{C}_{18:1}$ with nss-SO_4^{2-} (oxidation product of DMS and MSA) are 0.79, 0.77 and 0.88, respectively. These results strongly support that LFAs are derived from marine source rather than continental source. It is clear that historical trends of MSA^- and nss-SO_4^{2-} are similar (except for 1930s) ($R=0.85$). Interestingly, both nss-SO_4^{2-} and MSA^- somewhat follow the δD record from Kamchatka (Figure 5f) (Sato et al., 2014), further supporting that these ions along with fatty acids are coupled with past climate change.

Historical trend of δD records in the Kamchatka ice core represents surface temperature for 1958-1996 and extended the reconstructed sea surface temperature from 1854 to 1995 (Sato et al., 2014; Smith et al., 2008). Historical δD data is also an indicator of changes in atmospheric transport of moisture, rainfall, and snowfall seasonality and humidity source (Dansgaard, 1964), which are essential factors for emission and deposition of fatty acids. For example, water vapor transport analysis showed that almost 80% of winter and 50% of summer precipitations over the Eurasian Continent originate from the North Pacific Ocean (Numaguti, 1999), which

can support the southern Alaskan atmospheric circulation (*Yasunari and Yamazaki, 2009*).

It should be noted that this δD record of ice core signal has a positive relation with mid-latitude North Pacific (20-30° N) surface temperature and negative correlation with sub polar North Pacific (40-50° N, 180-150° W) surface temperature. On the other hand, snow accumulation rate of Kamchatka has significant negative correlation with the sub polar North Pacific (40-60° N, 180-150° W) and significant positive correlation with the western coast of North America (40° N, 125° W and 60° N, 145° W). These two results indicate the extra tropical North Pacific surface climate conditions (*Sato et al., 2014; Smith et al., 2008*).

According to Sato et al. (2014), historical trend of δD in Kamchatka ice indicates the variations of climate oscillation such as Pacific Decadal Oscillation (PDO) and North Pacific Gyre Oscillation (NPGO). For instance, correlation coefficient (R) of annual mean of δD and NPGO (*Di Lorenzo et al., 2008*) is 0.70 ($p < 0.10$) after great climate shift (1979-1997). Moreover, δD records seem to correlate with extended reconstructed sea surface temperature of the mid to high latitude North Pacific (30-45° N, 165° E- 165° W), which can represent the sea surface temperature anomaly and PDO (*Sato et al., 2014, reference therein*). Relation between 15-point running mean (RM) of δD (15-RM δD) and 21-RM of $C_{18:1}/C_{18:0}$ showed a positive correlation ($R = 0.80$). It further suggests that photochemical aging is associated with the climate periodicity cycle. Interestingly, 15-RM of LFAs and 15-RM of δD showed a better correlation ($R=0.79$) as compared to 15-RM of HFAs (0.54), suggesting that sea-to-air emissions of LFAs are associated with the climate periodicity. These results indicate a significant atmospheric transport of air parcels from lower to higher latitudes in the North Pacific rather than the continental source regions in Alaska. Hence, historical

trend of fatty acids in ice core is a good indicator for changes in atmospheric circulation over the North Pacific, where PDO and NPGO seem to be important.

Similarly, Parkinson et al. (1999) reported the overall reduction of sea ice extent since 1978 to 1996, with somewhat extent for 1990-1996. Parkinson and Cavalieri, (2002) reported a 21-year microwave data set of Arctic regions and demonstrated that there is a reduction of sea ice extent at a rate of -2.7 ± 0.5 % per decade, in which summer rate is greater (-4.9 ± 1.5 %) compared to winter (-1.8 ± 0.6 %). In addition, National Snow and Ice Data Center (nsidc.org) and/or Alaska Ocean Observing System (www.aos.org) also reported that sea ice extent is declined from 1978 to 2010 for the Northern Hemisphere. Following the declined sea ice extent in the Arctic region, we observed a distinct increase of LFAs in ice core during 1980-2000 (Figure 5c). Hence, fatty acids in ice core are likely linked to the atmospheric transport of plankton-derived organic matter emitted from the ocean.

Historical trends of LFAs and HFAs are somewhat similar to solar irradiance (e.g., Lean, 2000, 2010) and reconstructed Greenland temperature anomaly (GTA) (e.g., Kobashi et al., 2013), the latter primarily reflects Arctic Oscillations (AO) except for few points around AD 1870s (Figure 5c, d). Strong correlations between 30-RM of LFAs and 30-RM of GTA (0.86), and 21-RM of HFAs and 21-RM of GTA (0.86) suggest that long-range transport and deposition of LFAs and HFAs are linked to AO. This agreement further suggests that variability of LFAs and HFAs in the Alaskan ice core could be significantly controlled by large-scale atmospheric circulation in the Northern Hemisphere on a multi-decadal scale (Figures 3, 4 and 5a-d). Concentrations of LFAs and HFAs increase when AO shows an increased negative phase. It is likely that when the sinusoidal jet streams travel (ridge) over the Alaskan regions, they rapidly deliver the air parcels from southern part of Alaska (the Bering

Sea, western North Pacific, and/or East Asian regions) during negative AO phase, and gradually travels over the southwestern to southeastern part of North America (trough) due to the weakening of Icelandic low and Azores high pressure center (<http://www.nc-climate.ncsu.edu/climate/>). This result also reveals that the sea-to-air emission of fatty acids followed by subsequent transport to the APA site sensitively responds to the multi-decadal climatic periodicity cycle (e.g., PDO, NPGO and AO).

3.5. Conclusions

This study demonstrates that fatty acids are abundant in the Aurora Peak ice core (180 m long, 1734 - 2008) from southern Alaska. The molecular distributions of fatty acids were characterized by the predominance of C_{16:0}, followed by C_{18:1} and C_{14:0}. This distribution pattern is different from that of other ice core from Greenland Site-J where longer-chain fatty acids of terrestrial higher plant origin are often more abundant. Correlation analyses of LMW fatty acids with azelaic acid, major ions, levoglucosan and sugar compounds suggest that fatty acids are mainly derived by sea-to-air emissions of phytoplankton-derived organic matter in the northern North Pacific including the Gulf of Alaska. This study further demonstrates that fatty acids are strongly associated with climate periodicity cycle, which could be transported via atmospheric circulation in the circumpolar regions. Comparisons of fatty acid profiles in the ice core with paleoclimate proxy records such as Arctic Oscillation (AO) index and δD records in the ice core from Northeast Asia showed a strong agreement, suggesting that fatty acids in ice core can be used as useful indicators for the changes in marine biogenic inputs to Alaskan region.

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Table 1. Concentrations of homologous series of fatty acids (C_{12:0}-C_{30:0}) in the ice core from Aurora Peak, Alaska since 1665-2008.

Common Name	Formula	Abbr.	Concentrations (ng/g-ice)			
			Ave.	Min.	Max.	SD
Lauric acid	CH ₃ (CH ₂) ₁₀ COOH	C _{12:0}	4.82	BDL	21.6	4.65
Myristic acid	CH ₃ (CH ₂) ₁₂ COOH	C _{14:0}	15.3	BDL	91.3	21.9
Pentadecylic acid	CH ₃ (CH ₂) ₁₃ COOH	C _{15:0}	3.56	BDL	17.9	4.69
Palmitic acid	CH ₃ (CH ₂) ₁₄ COOH	C _{16:0}	20.3	BDL	95.1	29.8
Margaric acid	CH ₃ (CH ₂) ₁₅ COOH	C _{17:0}	5.29	BDL	59.2	10.7
Stearic acid	CH ₃ (CH ₂) ₁₆ COOH	C _{18:0}	10.7	BDL	84.3	17.8
Oleic acid	CH ₃ (CH ₂) ₇ CH=CH (CH ₂) ₇ COOH	C _{18:1}	19.6	BDL	188.9	38.6
Arachidic acid	CH ₃ (CH ₂) ₁₈ COOH	C _{20:0}	2.03	BDL	26.3	4.48
Behenic acid	CH ₃ (CH ₂) ₂₀ COOH	C _{22:0}	1.72	BDL	21.8	3.66
Tricosylic acid	CH ₃ (CH ₂) ₂₁ COOH	C _{23:0}	0.83	BDL	10.2	1.81
Lignoceric acid	CH ₃ (CH ₂) ₂₂ COOH	C _{24:0}	3.32	BDL	47.7	7.74
Pentacosylic acid	CH ₃ (CH ₂) ₂₃ COOH	C _{25:0}	1.02	BDL	12.4	2.27
Cerotic acid	CH ₃ (CH ₂) ₂₄ COOH	C _{26:0}	1.57	BDL	19.5	3.44
Heptacosylic acid	CH ₃ (CH ₂) ₂₅ COOH	C _{27:0}	0.36	BDL	1.48	0.41
Montanic acid	CH ₃ (CH ₂) ₂₆ COOH	C _{28:0}	1.09	BDL	9.41	2.16
Nonacosylic acid	CH ₃ (CH ₂) ₂₇ COOH	C _{29:0}	0.09	BDL	0.19	na
Melissic acid	CH ₃ (CH ₂) ₂₈ COOH	C _{30:0}	0.15	BDL	0.23	0.07

BDL= Below detection limit (0.001 ng/g-ice)

Figure Captions

Figure 1. Geographical location of Aurora Peak in Alaska, where 180-meter long ice core was drilled on the saddle of this peak in 2008.

Figure 2. Average molecular distributions of fatty acids ($C_{12:0}$ - $C_{30:0}$) in the ice core samples (age: 1665 – 2008) collected from Aurora Peak of Alaska.

Figure 3. Historical changes of selected low molecular weight fatty acids in the ice core collected from Aurora Peak in Alaska for 1665-2008.

Figure 4. Concentration changes of selected higher molecular weight fatty acids in the ice core from Aurora Peak in Alaska for 1665-2008.

Figure 5. Concentration changes of (a) total fatty acids ($C_{12:0}$ - $C_{30:0}$), (b) higher molecular weight fatty acids (HFAs) (c) lower molecular weight fatty acids (LFAs), (d) Greenland temperature anomalies (GTA) calculated from Greenland temperature and the NH temperature (*Kobashi et al., 2013*), (e) concentration ratios of $C_{18:1}$ and $C_{18:0}$ in the ice core since 1665-2008 collected from Aurora Peak in Alaska, (f) 20-year running mean of hydrogen isotope ratios (δD) in ice core from Kamchatka Peninsula, Russia (*Sato et al., 2014*), and (g) ice core depth v.s. estimated year (*Tshushima et al., 2014*).

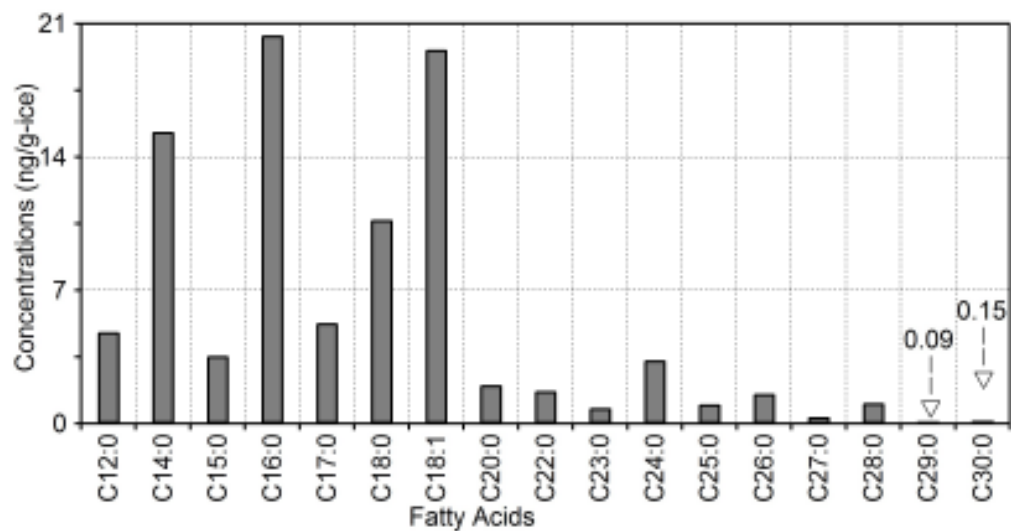


Figure 2. Average molecular distributions of fatty acids ($C_{12:0}$ - $C_{30:0}$) in the ice core samples (age: 1665 – 2008) collected from Aurora Peak of Alaska.

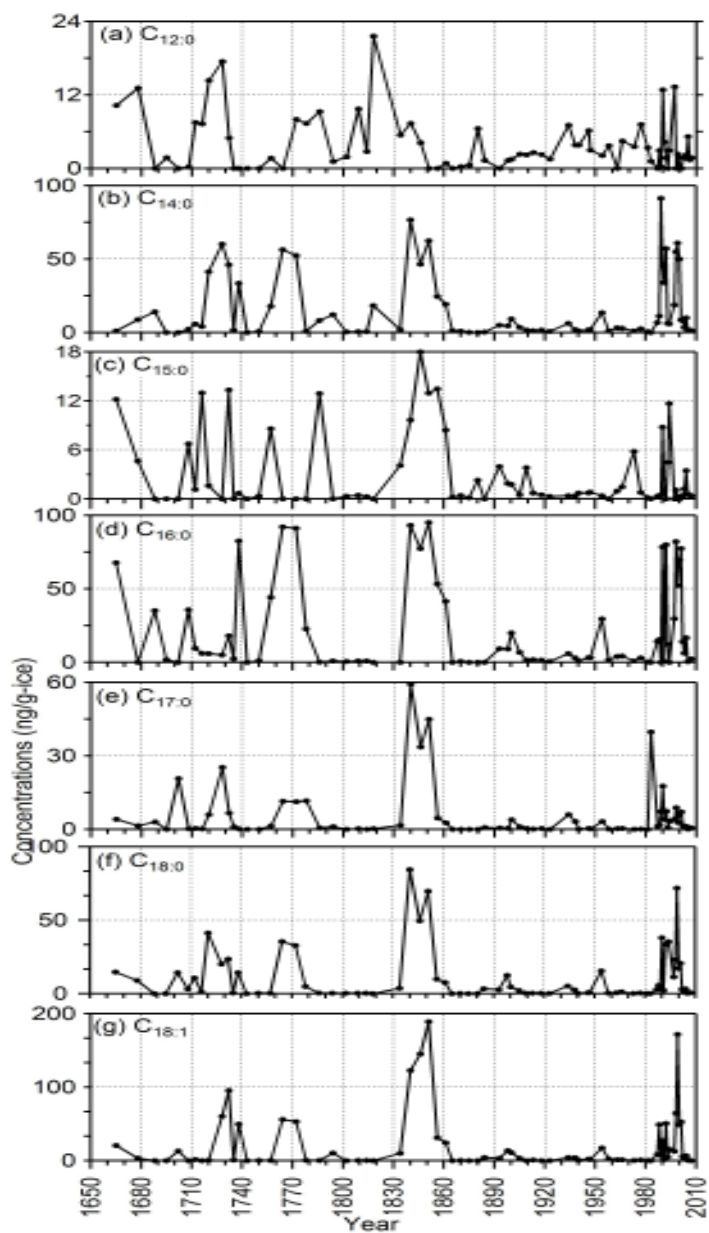


Figure 3. Historical changes of selected low molecular weight fatty acids in the ice core collected from Aurora Peak in Alaska for 1665-2008.

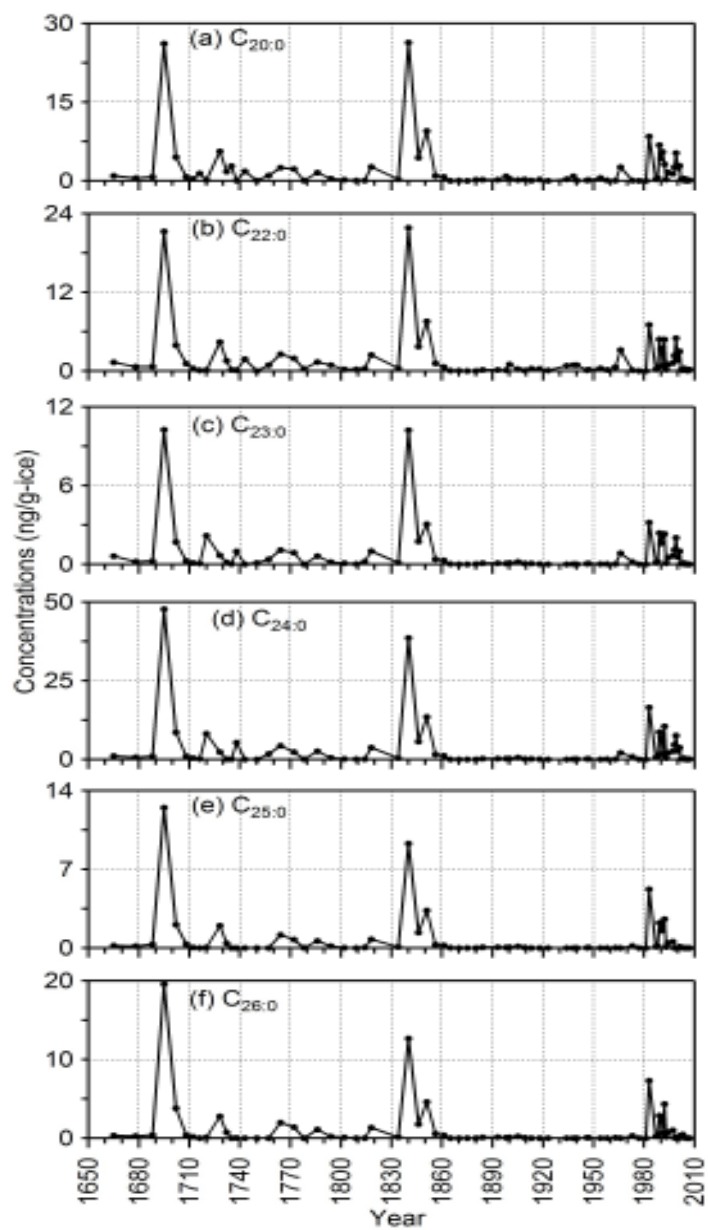


Figure 4. Concentration changes of selected higher molecular weight fatty acids in the ice core from Aurora Peak in Alaska for 1665-2008.

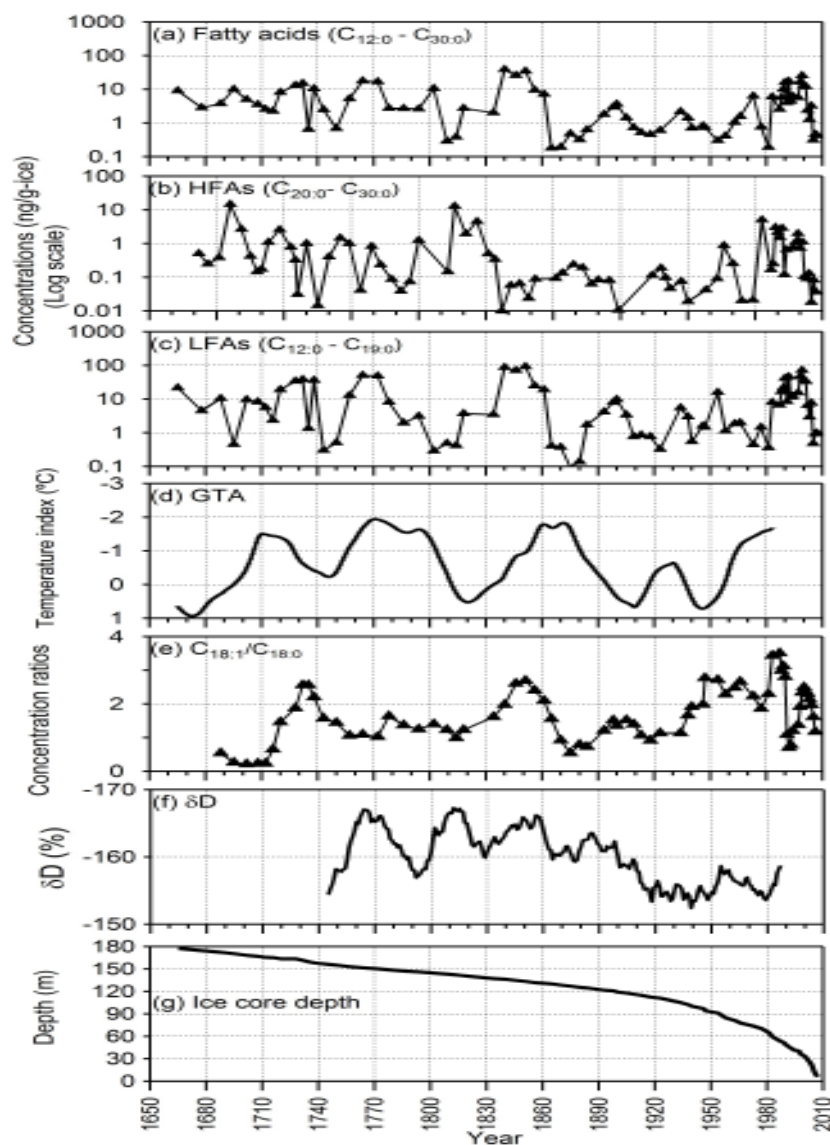


Figure 5. Concentration changes of (a) total fatty acids ($C_{12:0}$ - $C_{30:0}$), (b) higher molecular weight fatty acids (HFAs) (c) lower molecular weight fatty acids (LFAs), (d) Greenland temperature anomalies (GTA) calculated from Greenland temperature and the NH temperature (Kobashi et al., 2013), (e) concentration ratios of $C_{18:1}$ and $C_{18:0}$ in the ice core since 1665-2008 collected from Aurora Peak in Alaska, (f) 20-year running mean of hydrogen isotope ratios (δD) in ice core from Kamchatka Peninsula, Russia (Sato et al., 2014), and (g) ice core depth v.s. estimated year (Tshushima et al., 2014).

Chapter 4: Ice core records of biomass burning organic tracers in the Aurora Peak of Alaska since 1660s: Implications for forest fire activities in the Northern Hemisphere

4.1. Introduction

Ice core records provide the long-term changes in deposition and concentration of biomass burning organic (e.g., formate, acetate, dicarboxylic acid, pyruvic acid and α -dicarbonyls) and inorganic (e.g., NH_3^+ , SO_4^{2-} , NO_3^- and NO_2^-) atmospheric chemical species, which are reported elsewhere (*Wolf et al., 2012; Kawamura et al., 2012; Lamarque et al., 2010; Kaufmann et al., 2010; Andreae and Merlet, 2001; Legrand and Mayewski, 1997; Yang et al., 1995*). Biomass burning activities (forest fires and residential heating) have some extent on climate change effect (e.g., *Kawamura et al., 2012; Keywood et al., 2011; Whitlow et al., 1994*). Many study showed that there are some discrepancy of temporal and spatial biomass burning activities (e.g., *Kawamura et al., 2012; Yalcin et al., 2006; Whitlow et al., 1994; reference therein*) in the Northern and Southern Hemisphere (NH/SH).

They showed different atmospheric transport pattern from source region to sampling site of different ice core records (*Whitlow et al., 1994*), which can alter the glacio-chemical cycle in the NH and SH. In contrast, there is a few study of specific organic tracers of biomass burning for an ice core, e.g., levoglucosan (1,6-anhydro- β -D-glucopyranose), which is pyrolysis product of cellulose and hemi cellulose (*Kawamura et al., 2012*), dehydroabietic (1-phenanthrenecarboxylic acid) and vanillic acid (4-hydroxy-3-methoxybenzoic acid) and other compounds (e.g., mannosan, and galactosan) in the NH.

Kawamura et al. (2012) reported first time these specific biomass burning tracers, e.g., levoglucosan, dehydroabietic and vanillic acid for an ice core (AD 1693-1997), collected from Kamchatka-Peninsula, the Russia (56°04'N, 160°28'E, Elevation: 3,903 m), western North Pacific Ocean.

This time, we report, same compounds (e.g., levoglucosan, dehydroabietic and vanillic acid) for an ice core, which is collected from the Aurora Peak of southern Alaska (APA), eastern North Pacific Ocean, since 1665-2008 to better understand the historical atmospheric transport variability between western North Pacific (*Kawamura et al., 2012*) to eastern North Pacific region (this study) from source regions. Particularly, 10 day backward trajectory since 1992-2002 showed that southern Alaska can receive different air masses from the North Pacific Regions, East Asia, Eastern Russia-Siberia, higher latitudes of Alaskan regions, Japan, and Canadian regions in the troposphere (>300 hPa) (*Yasunari and Yamazaki, 2009*). Similarly, Kamchatka-Peninsula also can receive air masses from Siberia, Far East, North China and Eastern Europe (*Kawamura et al., 2012*).

4.2. Samples and Analytical Procedures

Total numbers of ice core sections were 147 (50 cm long, ¼ cut), i.e., sampling frequency was ~40% of 180 m deep ice core. These ice core samples (150 mL) were concentrated to almost dryness using a rotary evaporator under a vacuum in a pear shape flask (300 ml) and extracted by mixture of CH₂Cl₂/CH₃OH (2:1) using ultrasonic bath (*Kawamura et al., 2012*). The total dissolved and particulate organic matters were further eluted with CH₂Cl₂ and methanol to extract the organic compounds adsorbed on the particles as reported previously (*Kawamura et al., 2012; Fu et al., 2008; Simoneit et al., 2004*). The extract and eluents were transferred to 1.5 mL glass vial and again dried

under nitrogen stream. Extract were derivatized with 99% N, O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) +1%trimethylchlorosilane (TMCS) at 70° C for two hour^{2,18} (*Kawamura et al., 2012; Fu et al., 2008*). The derivatized fractions were further dissolved in n-hexane and peaks were identified by gas chromatography/mass spectrometry (GC/MS) using a capillary column (HP-5MS, 30 m × 0.32 mm I.D. × 0.25 µm film thickness) installed with a split/splitless injector (*Kawamura et al., 2012*).

Levoglucosan, dehydroabietic acid and vanillic acid were determined by comparing the authentic standard of GC/MS and mass spectral data of NIST/Willey library as external standards. More details are reported elsewhere (*Kawamura et al., 2012; Fu et al., 2008; Simoneit et al., 2004*). We conducted triplicate analyses for real sample to check the uncertainty of concentrations. The uncertainty of levoglucosan, dehydroabietic and vanillic acid were 6.72, 0.74 and 2.40, respectively. Moreover, recoveries of target compounds were satisfactory (better than 85%). Similarly, Aliquots of melt water (10 mL) were used to analyze water-soluble organic carbon (WSOC) as reported elsewhere (*Kawamura et al., 2012; Kunwar and Kawamura, 2014a, b*).

4.3. Result and Discussion

Anhydro-monosaccharides can lead an important fraction of water-soluble organic carbon (WSOC), which is produced from the pyrolysis and/or combustion of cellulose and/or hemi cellulose containing biomass from wildfires and domestic wood fires (*Simoneit, 2002*) at temperatures above 300 °C (*Simoneit et al., 2002; Fraser and Lakshmanan, 2000; Shafizadeh, 1984*). Many study showed that levoglucosan (C₆H₁₀O₅) is the most abundant anhydro-monosaccharide (*Kawamura et al., 2012; Simoneit, 2002*;

Kuo et al., 2011; Engling et al., 2006; Hoffmann et al., 2010), which is tracked by other concentrations of anhydro-monosaccharide, e.g., mannosan (1,6-anhydro- β -D-mannopyranose; $C_6H_{10}O_5$), galactosan (1,6-anhydro- β -D-galactopyranose; $C_6H_{12}O_6$) and/or dehydroabietic acid ($C_{20}H_{28}O_2$). Such type of specific factors and the sources (i.e., distribution) can make levoglucosan a unique tracer (*Jordan et al., 2006; Simoneit et al., 1999*) in the source regions of southern Alaska because saddle of the Aurora Peak is far from the biomass burning source regions as shown in Figure 1.

4.3.1. Levoglucosan

This study showed 8.6 times higher concentration of levoglucosan (range: BDL-20802, average: 542 ± 2343 ng/L) compared to dehydroabietic (range: BDL-555, ave. 62 ± 97.2 ng/L) and more than three hundred times higher than vanillic ($C_8H_8O_4$) acid (range: BDL-18.5, ave. 1.36 ± 3.03 ng/L) since 1665-2008. It should be noted that combustion of lignite (lignite include fossilized cellulose), i.e., combustion of hemicellulose emits levoglucosan and its isomers, i.e., e.g., mannosan and galactosan (*Kuo et al., 2011; Hoffmann et al., 2010*). We didn't detect these isomers compound of levoglucosan as a significant concentration for this study. In contrast, many aerosol samples showed significant concentrations of these isomers and levoglucosan (i.e., anhydrosugars), reported elsewhere. For instance, all aerosol samples of "round-the-world cruise (*Fu and Kawamura et al., 2011*), Mt. Tai, North China Plain (*Fu et al., 2008*) and urban aerosol in tropical India (*Fu et al., 2010*).

Higher ratios of levoglucosan (L) and mannosan (M) indicate deciduous forest fires activities (*Kawamura et al., 2012*). For instance, Kawamura et al. (2012) reported very

lower ratios of L/M (range: 3.3 – 5.0) for an ice core of Kamchatka compared to lignite burning (30-90) at 200° C (*Kuo et al., 2011*) and aerosols samples of Gosan site in south Korea (15-40, ave. 21) (*Simoneit et al., 2004*) suggest gymnosperm sources for anhydrosugars (*Kawamura et al., 2012*). Hence, we cannot discuss more about deciduous forest fires activities in the source regions of southern Alaska.

Insignificant concentration of mannosan and galactosan indicate that, combustion of lignite burning in the source regions of southern Alaska was minor. These result suggest that, contribution of combustion of lignite burning in the East Asia, Eastern Russia, Siberia, higher latitudes of Alaskan regions, Japan, and Canadian regions to the ice core site was insufficient. In contrast, western North Pacific ice core records from Kamchatka, Peninsula (*Kawamura et al., 2012*) showed these anhydrosugars, suggest that western North Pacific region and eastern North Pacific region could be influenced by different air mass chemistry (e.g., lignite burning plume did not influence the southern Alaskan glaciers) corresponding to other BB tracers. It should be noted that Kamchatka, Peninsula's ratio of levoglucosan and mannosan (L/M) range was close to gymnosperm (conifer) burning. This evidence suggests that lignite burning didn't alter the Alaskan glacier's chemistry since 1665-2008.

It should be noted that degradation fluxes of levoglucosan in cloud droplets and aqueous particles (deliquescent particles) are reported recently, which can be oxidized by OH radical in the tropospheric aqueous phase, where as mean degradation fluxes was in around 7.2 ng m⁻³ h⁻¹ in summer and 4.7 ng m⁻³ h⁻¹ in winter season (*Hoffmann et al., 2010*). Hence, we can speculate that levoglucosan could be more stable compared to isomers compound (*Fraser and Lakshmanan, 2000; Hoffmann et al., 2010*) during long-

range atmospheric transport from source points to southern Alaska. Moreover, stability of levoglucosan is further confirmed in a aerosol chamber study with atmospheric lifetime of 0.7-2.2 days in summer season (*Hennigan et al., 2010*). These results demonstrate the biomass burning emissions in source apportionment for saddle of APA.

Levoglucosan showed higher concentrations in around 1660s-1830s (Figure 2a) with sporadic peaks in 1678 (ice core depth in meter: 174.6 and concentration 593 ng/L), 1692 (172.2m; 704 ng/L), 1695 (170.3m; 1250 ng/L), 1716 (165.6m; 990 ng/L), 1750 (156.7m; 913 ng/L), 1764 (151.5m; 1433 ng/L), 1786 (147.3m; 7057 ng/L), 1794 (146.1m; 3302 ng/L) and 1834 (138.4m; 944 ng/L) than its background level (542 ng/L). These higher spikes could be related to forest fires activities in the source regions of southern Alaska. Source regions could be East Asia, Eastern Russia, Siberia, higher latitudes of Alaskan regions, Japan, and Canadian regions (*Yasunari and Yamazaki, 2009*). For instance, Ivanova et al. (2010) reported frequency of heavy forest fires (e.g., boreal forest) activities in spring, summer and autumn in the eastern Siberia, which is the potential source of Alaska (*Yasunari and Yamazaki, 2009*). This study showed higher concentrations of levoglucosan before 1840s (Figure 2a). Marlon et al.(2008) further confirmed that there was heavy biomass burning between 1750s -1840s in a global scale, which is linked to increasing anthropogenic activities (e.g., population growth and land-use change).

Similalry, we detected higher spikes in 1898 (120.7m; 577 ng/L), 1913 (114.8m; 20802 ng/L), 1966 (77.7m; 692 ng/L) and 2005 (13.7m; 598 ng/L) than its background level (542 ng/L). Figure 2a clearly showed that there is lower concentration after 1830s (except, for 1898, 1913, 1966 and 2005) it could be attributed to a intensive garzing,

agriculture and forest fire management (Marlon *et al.*, 2008; Eichler *et al.*, 2011). It should be noted that charcoal signals are scarce for Siberian regions compared to Northern America and European ice core records (Eichler *et al.*, 2011). We did not detect significant concentrations of any isomers as we have discussed above. Moreover, two thirds of Earth's boreal forest (17 million km²) lies in the Russia, which is a potential source of forest fires signal of global scale (Isaev *et al.*, 2002).

Mt. Logan Canada, GISP2 and 20D (older than 1850s) ice core records of Greenland are characterized by higher spikes of NH₄⁺ and superimposed on a relatively uniform in summer time and minimum in wintertime (Whitlow *et al.*, 1994) suggest that they have common source regions in the circumpolar regions. We got higher spikes of levoglucosan before 1840s (Figure 2a), which is similar to higher spikes of NH₄⁺ since 1770-1790, 1810-1830 in the Mt. Logan suggest the similar source regions of different sampling sites. In contrast, Mt. Logan showed higher spikes in the intervals 1850-1870 and 1930-1980, which is dissimilar (except, for a two points) to this Aurora Peak (Figure 2a). It should be noted that Greenland records (GISP2 and 20D) showed lower spikes compared to Mt. Logan (Whitlow *et al.*, 1994) during these intervals (i.e., 1850-1870 and 1930-1980), which is similar to saddle of Aurora Peak (except for 1966) suggest the similar source regions (Whitlow *et al.*, 1994; Davidson *et al.*, 1993; Holdsworth *et al.*, 1992). The potential source regions of Greenland are northern North America, Europe and Siberia. Similarly, Siberia, Alaska and British Columbia are a likely source for Mt. Logan (Whitlow *et al.*, 1994; Davidson *et al.*, 1993; Holdsworth *et al.*, 1992).

Moreover, except for a few points, e.g., 1999 (436 ng/L) and 2005 (598 ng/L) concentration is drastically decreased since 1980-2008 suggest that forest fires activities

could be controlled by many factors. For instance, Central and East Siberian forest fire activities were controlled by strong climate periodicity e.g., Arctic Oscillation (AO), El Nino, intensification of the hydrological cycle in the central Asia and other human activities in the NH (*Eichler et al., 2011; Achard et al., 2008; Balzter et al., 2007; Wallenius et al., 2005*). Moreover, Eichler et al. (2009) further confirmed that higher concentrations of NH_4^+ and HCOO^- between 1816-2001 were emitted from direct biogenic emission rather than biomass burning (*Olivier et al., 2006*) in the Belukha glacier in the Siberian Altai mountains. Similarly, low concentration of charcoal between 1700-2000 in this Altai mountain further suggest that forest fire activities were active compared to other anthropogenic activities in the source regions (*Eichler et al., 2011*).

Similarly, sparsity spikes after 1910s in the Greenland (GISP2 and 20D) suggest low intensity of biomass burning and/or largely scavenged before reaching Greenland from the North America (Whitlow et al. 1994), which is similar to saddle of Aurora Peak, except for 1910 (20802 ng/L) may be due to point source around Alaskan region. Higher spikes of NH_4^+ is likely sources of Mt. Logan during 1900-1990 are central and eastern Siberia (*Robock, 1991*), which is dissimilar to this study, except for 1966 (2005 ng/L) suggest that local biomass burning is also important for southern Alaska.

Above results and discussions suggested the subsequent evidences: (a) heavy biomass burning could be activated in the source regions, (b) short range air mass circulation could be reached quickly to the southern Alaska, and enhanced the higher concentration of levoglucosan (c) dilution and/or scavenging of the biomass plume in the enroute could be maximum after 1830s (d) thus, biomass burning plume (e.g., same ice core records of SO_4^{2-} , NO_3^- , NH_4^+ showed significant concentration during same periods) could be

deposited significantly by short range atmospheric circulation in the exposed surface area of the glaciers that occur in summer time in the Northern Hemisphere, likely to be possible. These special events further suggest that Alaskan glacier can not preserve all most all biomass burning events in the circumpolar regions corresponding to biomass burning tracers that occurred in the source regions of the North Pacific (e.g., Siberian and North American source regions).

Hence, these historical records of levoglucosan suggest the heavy forest fires evidences before 1830s during long range atmospheric transport rather than short range transport are imprinted. For instance, forest fires intensity in 1660s-1830s could be in drought seasons by lightning in the Siberian regions as well as extensive burning to clear land for agriculture purpose in the northern Hemisphere (*Whitlow et al., 1994, reference therein*). Suppressing of concentrations trends after 1830s (except for few points) showed that source could be changed significantly and/or forest fire activities could be suppressed and/or controlled after 1830s-1980s (*Whitlow et al., 1994*). It should be noted that mid to late 1800s are to be considered to be the Little Ice Age (*Mayewski et al., 1993*). Moreover, recent changes of the concentration trends in the Alaskan source regions is thought to be climate driven (*Whitlow et al., 1994, reference therein*).

4.3.2. Dehydroabietic Acid

Dehydroabietic acid is produced by pyrolytic dehydration of abietic acid from conifer resin (*Kawamura et al., 2012; Simoneit et al., 1993*). It can be used as a specific biomass-burning tracer for conifer trees for an ice core study. We detected second dominant concentration of dehydroabietic acid (range: BDL-555, ave. 62.4 ± 97.2 ng/L), which is

8.69 times lower than levoglucosan and more than 46 times higher than vanillic acid (range: BDL-18.5, ave. 1.36 ± 3.03 ng/L). Dehydroabietic acid showed higher spikes in 1678 (ice core depth in meter, i.e., 173.9m; 200 ng/L), 1716 (165.3m; 67.5ng/L), 1728 (161.5m; 139 ng/L), 1732 (159.6.3m; 233 ng/L), 1738 (158.3m; 113 ng/L), 1750 (156.78m; 66.9 ng/L), 1764 (151.5m; 331 ng/L), 1786 (147.3m; 386 ng/L), 1794 (146.1m; 78.6 ng/L), 1913 (114.8m; 101 ng/L) and 1994-1999 (depth is 44.8-5.92m) has 92.8, 199, 141, 203, 136, 109, 98.4, 124, 174, 121, 298 and 555, respectively. These periods are similar to higher spikes of levoglucosan, except for a few points (e.g., 1734-1738) before 1990s (Figure 2a, b). Historical concentration trend is also similar to levoglucosan concentration trend before 1980s, which is near about similar to Kamchatka ice core records. In contrast, Kamchatka showed gradual increase of dehydroabietic acid (Figure 2b) after 1950s (*Kawamura et al., 2012*). These result suggest that biomass burning plume of pine, larch, spruce and fir trees in Siberian regions (*Kawamura et al., 2012; Ivanova et al., 2010*) could not be reached southern Alaska significantly compared to Kamchatka.

Hence, higher concentration of dehydroabietic acid after 1980s compared to levoglucosan, which is similar to Kamchatka records further suggest that biomass burning plume from boreal conifer trees could be transported to the North Pacific regions may be from Siberian regions (*Kawamura et al., 2012*). It also suggest that East Asian regions (e.g., broad-leaf trees are common) could be also important for levoglucosan rather than dehydroabietic acid (boreal forest fires in Siberia, i.e., pine trees). It should be noted that Alaska can receive different air masses from the East Asia, Eastern Russia, Siberia, higher latitudes of Alaskan regions, Japan, and Canadian regions in the troposphere

(>300 hPa) (*Yasunari and Yamazaki, 2009*) and Kamchatka-Peninsula also can receive air masses from Siberia, Far East, North China and Eastern Europe (*Kawamura et al., 2012*).

These results showed somewhat similarity between levoglucosan records of Kamchatka and Alaska (except for few points) and somewhat discrepancy between dehydroabietic acids between these sampling sites. Kamchatka showed gradual increase after 1950s meanwhile Alaska showed after 1980s suggest that conifer-burning plume could not be transported significantly to the southern Alaska rather than Kamchatka since 1950s – 1980s. It has also another possibility for this discrepancy of Kamchatka and Alaska, e.g., 1950s – 1980s that dehydroabietic acids could be decomposed during long-range transport (*Kawamura et al., 2012; Simoneit and Elias, 2001*) before reaching and scavenging from Siberian regions to southern Alaska (i.e., eastern North Pacific ice core) compared to Kamchatka (i.e., western North Pacific). Particularly, Kamchatka ice core also doesn't show higher spikes (except, 1970) since 1950s- 1970s compared to before and after during these decades. Hence, such type of lower spikes and/or sporadic peaks of levoglucosan and dehydroabietic acid suggest that source regions should be different (e.g., east Asian broad leaf trees and Siberian source, e.g., boreal forest/pine trees) and long range atmospheric transport is important for this historical concentration trends of dehydroabietic acid rather than levoglucosan over the saddle of Aurora Peak.

4.3.3 Vanillic Acid

We detected vanillic acid (VA) concentrations (Figure 2c), which is a biomass burning tracers of lignin (*Kawamura et al., 2012; Simoneit et al., 1993*) for an ice core of the Aurora Peak (Figure 2c). Particularly, VA can be produced by incomplete combustion of conifer trees (*Simoneit et al., 1993*). Figure 2c show sporadic peaks of lignin in 1672 (2.23 ng/L), 1678 (3.25 ng/L), 1692 (3.23 ng/L), 1695 (5.56 ng/L), 1698 (1.50 ng/L), 1732 (3.98 ng/L), 1764 (1.56 ng/L), 1786 (3.65 ng/L), 1794 (1.35 ng/L), 1814 (11.0 ng/L), 1818 (5.50 ng/L), 1913 (2.12 ng/L), 1973 (5.52 ng/L), 1992 (2.56 ng/L), 1993 (5.66 ng/L) and 2004-2007 (2.07, 18.5, 7.27 and 12.6 ng/L, respectively. We got similar higher spikes of VA and levoglucosan during these periods (except for few points, e.g., 2004, 2006 and 2007). Similarly, Kamchatka ice core showed similar type of higher spikes each other, except few point (e.g., 1972 and 1992). Similarity of higher spikes suggest that biomass combustion sources (e.g., woody parts of trees) and source regions could be similar (*Kawamura et al., 2012*), i.e., lignin and cellulose source regions of southern Alaska were significant simultaneously. Moreover, it also indicates that long range transport were important for VA and levoglucosan compared to dehydroabietic acid for southern Alaska. It should be noted that we did not detect *p*-hydroxybenzoic acid (*p*-HBA), which can be produced from incomplete combustion of grasses (*Kawamura et al., 2012; Simoneit et al., 2002*). This result suggest that long-range atmospheric transport was insignificant, which could be somewhat similar to dehydroabietic acid compared to atmospheric transport of levoglucosan as we have discussed above sections. In other words, dehydroabietic acids and *p*-HBA could be more unstable compared to photo-degradation of levoglucosan during long range transport. For instance, higher sensitivity

of dehydroabietic acid were reported compared to levoglucosan (*Simoneit et al., 2002; Simoneit and Elias, 2001*). We detected significant concentrations of dehydroabietic acid since 1665-2008 (Figure 2b). Hence, we may speculate that *p*-HBA could be more unstable compared to levoglucosan, dehydroabietic and vanillic acid.

4.4. Comparison with Ammonium, Nitrite, Nitrate and Sulfate

Ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}) were used to know the better understanding of atmospheric signal of biomass burning and/or Pioneer Agriculture Revolution (PIA-GREV) in the NH, which are reported elsewhere (*Holdsworth et al., 1996, Legrand and Mayewski, 1997, references therein*). For instance, signal of biomass burning (e.g., NH_4^+) comes from ammonium gas (e.g., $[\text{NH}_4]_2\text{SO}_4$) in snow particles, which is a constitute of forest fire smoke (*Holdsworth et al., 1996, references therein*). Similarly, levoglucosan is a unique biomass burning tracer (*Simoneit, 2002*). In contrast, correlation of levoglucosan with NH_4^+ ($R = 0.03$), NO_3^- (0.03), sulfate SO_4^{2-} (0.15) and NO_2^- (0.17) from the same ice core (unpublished data) strongly suggest that NH_4^+ , NO_2^- , NO_3^- and SO_4^{2-} may not represent pristine biomass burning signal at least in the Aurora Peak.

4.5. Conclusions

Levoglucosan (ave. 543 ± 2343 ng/L), dehydroabietic (ave. 62.4 ± 97.2 ng/L) and vanillic acid (1.36 ± 3.03 ng/L) are present in the saddle of Aurora Peak, has been reported to better understand temporal trends of biomass burning activities in the source region of southern Alaska. Levoglucosan showed sporadic peaks during the 1660s-1830s, 1898, 1913, 1966 and 2005. Dehydroabietic and vanillic acid showed similar historical trends with levoglucosan at least before 1980s. Historical trends of levoglucosan, dehydroabietic acid and vanillic acid showed that biomass burning activities from resin, and lignin boreal conifer trees and other higher plant, and grasses were significant before 1830s and after 1980s in the source regions of southern Alaska. Correlation of levoglucosan with NH_4^+ ($R = 0.03$), NO_3^- (0.03), sulfate SO_4^{2-} (0.15) and NO_2^- (0.17) from the same ice core suggest that these anions and cations can not represent the gleaming signal of biomass burning activities in the source regions for the southern Alaska. These results further suggest that forest fires signal in the NH dependent on the source regions and ice core sampling sites. Hence, it inquires about the long-range and/or short-range atmospheric transport, which will be important for biomass burning tracers (i.e., levoglucosan, dehydroabietic and vanillic acid) and cations, and anions.

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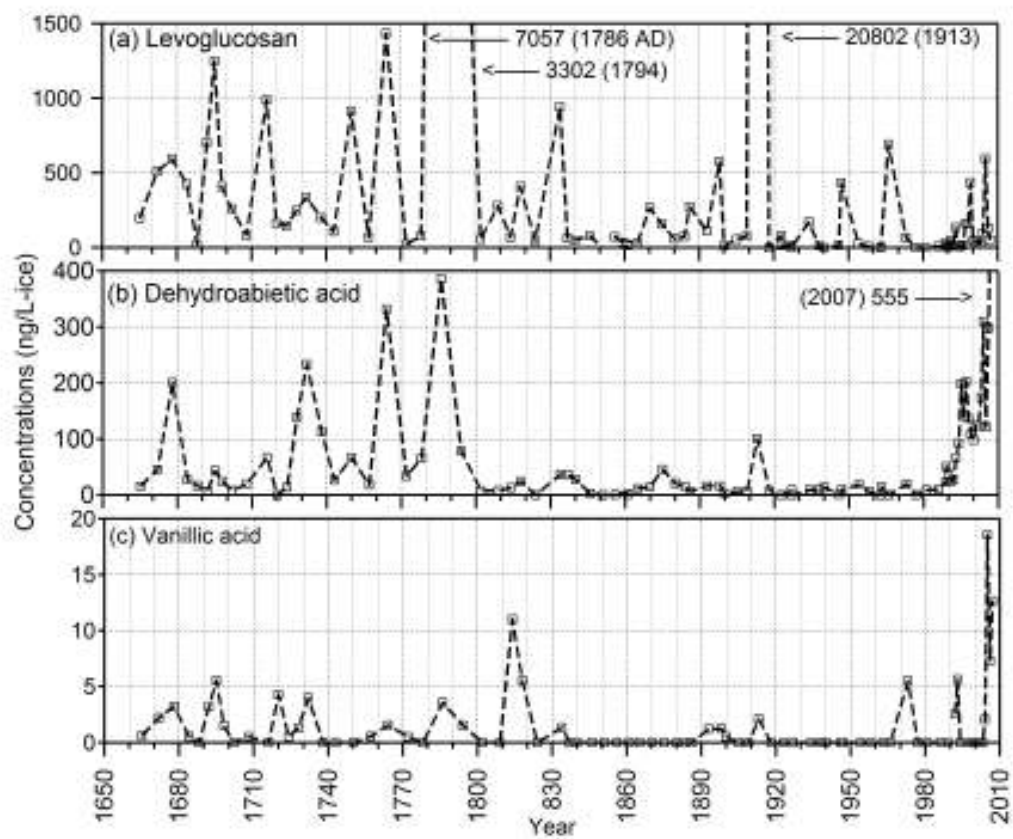


Figure 2: Concentration changes of levoglucosan, dehydroabietic and vanillic acid in the ice core from Aurora Peak in Alaska for 1665-2008.

Chapter 5: The pristine atmospheric signal recorded in NO_2^- , NO_3^- , SO_4^{2-} and methanesulfonate (CH_3SO_3^-) from the Aurora Peak of Alaskan ice core records (1734-2008): Climate change implications

5.1. Introduction

Northern latitudes comprise different types of climate throughout the year and many multi-decadal atmospheric circulation, soils exhalation and/or frequent wind erosion, vegetations, volcanism and human activities are sources of aerosols. These factors contribute anthropogenic and biogenic aerosols for an ice core in the North Pacific region. Particularly, these natural and industrial activities have lead to an increase in the concentrations of nitrogen species (NO_x); nitrate (NO_3^-) and nitrite (NO_2^-), sulfur species; sulfate (SO_4^{2-}), and methanesulfonate acid (CH_3SO_3^-), which can represent the atmospheric tracers (*Kaufmann et al., 2010; Legrand and Mayewski, 1997; Yang et al., 1995*). Increasing human activities and /or industrial revolution in the Northern hemisphere (NH) have drastically altered the chemical composition of pristine atmospheric input (e.g., marine and terrestrial input), which are reported elsewhere (*Kaufmann et al., 2010; Legrand and Mayewski, 1997; Yang et al., 1995; Legrand and Delmas, 1985; Wake et al., 1993; Kang et al., 2000, 2003; Moore et al., 2006*). Moreover, polar glaciers represent zonal and meridional atmospheric transport (sea-air-land interaction) and avenues of glaciochemistry over the NH (*Kaufmann et al., 2010; Moore et al., 2006; Silvente and Legrand, 1993; Kekonen et al., 2005; Kaspari et al., 2008, 2009*). Hence, polar glaciers are the proxy records of past atmospheric chemistry and the

climate of the Earth.

Here we have reported NO_2^- , NO_3^- , SO_4^{2-} and methanesulfonate (MSA^-) to better understand the high latitude glaciochemistry over an Alaskan region, making proxy records of past atmospheric chemistry and atmospheric transport, sources and transformation processes since the 1660s. These species are discussed in terms of past change of the polar glaciochemistry in the northern North Pacific.

5.2. Samples and Analytical Procedures

An ice core (180 m deep, 343 years old) was drilled in an ice cap in the saddle of Aurora Peak in Alaska (APA), which is situated in southeast Alaska (63.52°N; 146.54°W, elevation: 2,825 m) and surrounded by the Arctic Ocean (AO), Pacific Ocean (PO) and Bering Sea (Figure 1). The ice core was divided into ~50 cm and direct transported to the laboratory of the Institute of Low Temperature Science (ILTS), Hokkaido University, Japan and stored in a dark cold room at -20°C until analysis. The ice core chronologies were determined by using annual counting of hydrogen isotopes (δD) and Na^+ seasonal cycles. Age control was provided by referencing the horizon of tritium peaks in 1963 and 1964 (*Tshushima, 2011; Tsushima et al., 2014*). These ice core samples were shaved off (~5 – 7 mm) on a clean bench in cold room at -15°C (*e.g., Pokhrel et al., 2014a, 2014b*) using a ceramic knife to avoid possible adsorption contamination during sample collection using the method previously reported (*Legrand et al., 1993; Savarino and Legrand, 1998; Kawamura et al., 1999, 2001*). These scraped samples were kept for 24 hours in a container in a standard clean room. Total number of ice core sections was 74, i.e., sampling frequency was ~20% of 180 m deep ice core.

We determined NO_2^- , NO_3^- , SO_4^{2-} and CH_3SO_3^- using an ion chromatograph (761 Compact IC, Metrohm, Switzerland) reported elsewhere (*Miyazaki et al., 2011; Pavuluri et al., 2011; Kunwar and Kawamura, 2014*). Melted ice cores were filtrated using a membrane disc filter (Millex-GV, 0.25 μm , Millipore) and injected to Compact IC for major ions. 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 at a flow rate of 1.2 mL min^{-1} as an eluent and 40 mM H_2SO_4 for suppressor were used to determine anions. The detection limit for anion was 0.006 to 0.02 ng/L (*Kunwar and Kawamura, 2014*). The uncertainties in triplicate analyses of laboratory standards were within 0.02 to 13.2% for these anions. Here we report all concentrations of anions after the laboratory blank correction.

5.3. Results and Discussion

5.3.1. Historical Concentration Changes of NO_3^-

Many studies of ice core records indicate the industrial revolution, and human and atmospheric activities (e.g., cyclonic activities) in the Southern (SH) and Northern Hemispheres (NH) over many centuries (*Kaufmann et al., 2010; Legrand and Mayewski, 1997; Kang et al., 2000; Kaspari et al., 2007; Grigholm et al., 2009; Goto-Azuma and Koerner, 2001; Legrand and De Angelis, 1996*). Nitrate (NO_3^-) can be considered as a terrestrial source in the fresh snow and ice core (*Legrand and Mayewski, 1997; Wake et al., 1993; Moore et al., 2006; Kang et al., 2000, 2003*) and could be from fossil fuels' combustion, lightning, photooxidation of NO and exhalation of soils (*Yang et al., 1995; Legrand and Klirchner, 1990; Logan, 1983; Mayewski et al., 1990*;). In addition, galactic cosmic rays, biomass burning and oxidation of ammonia and N_2O can also contribute

nitrate (Yang *et al.*, 1995; Levy *et al.*, 1980; Mayewski and Legrand, 1990). Similarly, wet and dry atmospheric deposition (Baker *et al.*, 2003), physical transport of nitrate i.e., aeolian transport and deposition (Williams *et al.*, 2006), nitrogen fixation by diazotrophic organisms (Mahaffey *et al.*, 2005), the denitrification process (Dittmar and Birkicht, 2001) for open ocean water (e.g., change in nutrients in the oceans favor organisms). Nitrate could be formed and released from peroxyacetyl nitrate (PAN) due to high elevation in the free tropospheric environment (Goto-Azuma, 2001) creating a limiting factor and source of nitrate in the polar regions (Williams *et al.*, 2006; Gruber and Sarmiento, 2002; Duce *et al.*, 2008, 2009).

There are some sporadic peaks of NO_3^- in 1966 (23.8 ng/g), 1991 (32.0 ng/g), 1994 (30.7 ng/g), 2002 (17.7 ng/g), 2003 (17.1 ng/g), 2004 (29.2 ng/g), 2006 (27.0 ng/g) and 2007 (25.3 ng/g) compared to its background level from 1665-2008 (range: BDL-32.0, ave. 12.6 ± 7.11 ng/g-ice). Nitrate could be incorporated into the snow (Yang *et al.*, 1995; Legrand and Mayewski, 1997; Mayewski and Legrand, 1990) and its annual trends can show the source of a precursor in the Alaskan regions. The historical trend of NO_3^- (Figure 2a) is consistent since the 1660s-1980s compared to other anions (Figure 2b, d, e), except for some points (e.g., 1750, 1824, 1946 and 1966), and somewhat increasing trends after 1990-2008 suggesting that source regions, pathways and emission strength could not be changed significantly before the 1980s. In contrast, southern Greenland-Dye-3 (Mayewski *et al.*, 1990; Goto Azuma, 2001), Central Greenland-Summit (Legrand and De Angelis, 1996), 20D, and GISP2 showed higher spikes than their background levels after the 1940s (Goto- Azuma and Koerner, 2001; Yalcin and Wake, 2001). Similarly, Penny Ice Cap, Agassiz Ice Cap, Baffin Island in the Canadian low Arctic to

Canadian high Arctic regions, and Snofjellaafonna and Svalbard ice core records also showed higher spikes after the 1940s (*Goto-Azuma and Koerner, 2001; Yalcin and Wake, 2001*). Moreover, Dome C (*Legrand and Delmas, 1988a*) and the South Pole (*Mayewski and Legrand, 1990*) after the industrial revolution, and Vostok in the mid 1970s in the Dominion Range of the Antarctic ice core showed increasing historical trends in the southern hemisphere (*Mayewski and Legrand, 1990*).

In contrast, less pronounced summer spikes of nitrate at Mount Logan-Canada and Sentik Glacier-Himalaya revealed the pristine free tropospheric environment. Nitrate could be formed and released from peroxyacetyl nitrate (PAN) which might be due to the high elevation (e.g., 3017 m). These Mount Logan and Sentik Glacier areas can maintain some sunlight even in winter time suggesting that nitrate formed/released from PAN is deposited throughout the year (*Yang et al., 1995; Wake et al., 1993; Mayewski et al., 1993b; Monaghan and Holdsworth, 1990*). Hence, southern Alaska can represent the unique spatial and temporal atmospheric nitrate cycle in the North Pacific region of the 1660s – 2000s, since nitrate trends are more pronounced in the 1990s than previous decades (1660s-1980s). This further led us to determine the result of anthropogenic emission (including biomass burning) during long-range transport and local sources is to be expected after the 1990s. Moreover, NO_3^- could be re-emitted from snow sheet layers after deposition; this process would lead to consistency in NO_3^- distribution since 1660s-1980s. For instance, there is a large difference between the South Pole mean value of NO_3^- (ave. 102 ± 110 ng/g) and Vostok (ave. 16 ± 4 ng/g) before 1975, which is situated in the similar elevation of the Antarctic plateau (*Mayewski and Legrand, 1990*).

Moreover, the mean value of NO_3^- in the Dome C (ave. 19 ± 8 ng/g) and Dominion

Range (ave. 59 ± 12 ng/g) is also much lower than the concentration of the South Pole (ave. 102 ± 110 ng/g) (*Mayewski and Legrand, 1990*). This large difference of NO_3^- with respect to the South Pole could be associated with re-emission of NO_3^- from snow surface and a lower accumulation rate of snow fall (*Mayewski and Legrand, 1990*). Moreover, snow accumulation rate of GISP2 and 20D in Greenland, Mount Logan-St. Elias Range, Yukon-Canada, and Himalayas showed significant relation to nitrate flux (*Yang et al., 1995*). In contrast, the NO_3^- concentration trend of this study is consistent since 1660s-1980s (Figure 2a). Meanwhile, the snow accumulation rate of APA (8 mm year^{-1}) is increasing since 1900 and then drastically changes (23 mm year^{-1}) around 1976 (*Tsushima et al., 2014*).

The complex relation between nitric acid (HNO_3) and NO_3^- is reported elsewhere (*Rothlisberger et al., 2000, 2002; Abbatt, 1997; Thibert and Domine, 1998; Dibb et al., 1998; Honrath et al., 2000*). NO_3^- concentration was associated with the scavenging rate of HNO_3 in clouds, snow sheet, uptake and/or release of HNO_3 in snow surface. It should be noted that adsorption and desorption of HNO_3 is temperature dependent of the snow sheet (*Rothlisberger, et al., 2002*). The rate of photolysis of NO_3^- from the top few centimeters of snow surface is dependent upon the snow accumulation rate and exposed area under UV radiation. For example, many locations of Greenland and Antarctica (except for Dome C) showed decreasing trends in NO_3^- with increasing temperature (*Rothlisberger, et al., 2000*). Thus, photolysis could be more enhanced for Alaskan regions, but the gas-phase diffusion may be lower (*Rothlisberger et al., 2002*) due to higher pressure over the southern Alaskan regions compared to Greenland and Antarctica.

Moreover, there is somewhat inverse trends between NO_3^- and nss Ca^{2+} (not shown in figure) in the 1720s, 1830s and 1850s to 1950s; except for a few decades which suggest that acidic ice sheet's concentration of NO_3^- could be controlled and/or altered by calcium input, which is associated with terrestrial dust particles from the source regions (Rothlisberger *et al.*, 2000, 2002). This complex relation of Ca^{2+} , HNO_3 and NO_3^- interaction is reported elsewhere (Rothlisberger *et al.* 2000, 2002; Legrand *et al.*, 1999; Hanisch and Crowley, 2001). Thus, Alaskan NO_3^- trends and other polar sampling sites (SH and NH) are to be controlled by different factors (Rothlisberger *et al.*, 2000, 2002). Interestingly, these results suggest that NO_3^- concentration is independent on the snow accumulation rate of APA, being similar to Dome C and other studies of Antarctica (Legrand and Kirchner, 1990; Legrand and Delmas, 1986, 1988).

Mayewski and Legrand (1990) reported that there is some discrepancy of NO_3^- concentration's factors between SH and NH. For instance, biomass burning and deforestation affected 4-5 times the NO_3^- concentration in 1980-1985 of Rondonia in Brazil (Malingreau, and Tucker, 1988; Mayewski and Legrand, 1990). Major soluble ions of Mt. Geladaindongs (Tibetan ice core) showed an increasing concentration trend since the mid 1930s to 1970s and rapid change in the mid 1970s (Kaspari *et al.*, 2007; Grigholm *et al.*, 2009). The historical trends during those periods (mid 1930s to 1970s and mid 1970s) have been coupled with common source and common atmospheric transport pathways, and cyclonic activities, respectively (Kaspari *et al.*, 2007; Grigholm *et al.*, 2009). Moreover, NO_3^- concentration of APA (13.8 ng/g-ice) during the Great Climate Shift (1976 - 1977) in the NH (D'Aleo and Easterbook, 2010) is close to its background levels (e.g., 1960 – 2008; range: BDL – 32.0, ave. 14.5 ± 8.79 ng/g and 1665-

2008, ave. 12.6 ± 7.11 ng/g) suggesting that Great Climate Shift could not alter the NO_3^- concentration significantly over the APA.

The historical trend of NO_3^- is different than other species (e.g., NO_2^- , nss-SO_4^{2-} and NH_4^+) suggesting that there are different sources and/or different reactions (Figure 2a-f). Hence, consistency of historical higher spike periods suggest the similar sources regions and/or dust sources could be contributed at times of the year (may be seasonal effect) in the North Pacific. Thus, source of emission, atmospheric transport and accumulation trends in the NH and SH (including Brazilian locations) of NO_3^- are different compared to Aurora Peak of Alaska. This result further suggests that APA could be influenced by distinct atmospheric transport patterns different from other sampling sites of the NH and SH. It also retrieves pristine climate and pristine atmospheric transport since 1660s - 1980s with respect to NO_3^- concentration over the Aurora Peak of Alaska. Sampling site could not be significantly influenced by anthropogenic emission, which is completely different than other ice cores for both the Hemispheres. For instance, South Pole (*Legrand, M.; Mayewski, 1997*) and Svalbard ice cores (*Moore et al., 2006*) showed high concentrations of NO_3^- and SO_4^{2-} after the industrial revolution (1850s) and rapid rise after the heavily industrialized period of Siberia in the 1940s.

We did not detect any significant concentration changes before and after an industrial revolution compared to other ice core records in the NH and SH. Particularly, there are no increasing concentration trends even during 1900-1990. Hence, continental effects in the chemical composition of precipitated snow could be well related to the effects of aerosol transport away from the source regions (*Minikin et al., 1994*). Therefore, short range atmospheric transport may play an important role in the southern Alaskan region.

Even, these SO_4^{2-} , NO_2^- , NO_3^- and NH_4^+ (not shown in figure) have not shown any consecutive higher concentration during biomass burning periods in the NH during 1850s-1910s. Hence, NO_3^- also cannot represent vehicular emission and smokestacks at least before the 1980s.

We detected a significantly higher concentration of levoglucosan since 1680s-1840s compared to 1850s-1980s from the same ice core (unpublished data), which is a special tracer of biomass burning activities (*Kawamura et al., 2012*). This result also suggests that Alaskan precipitation was influenced by terrestrial sources of primary and secondary aerosol. But, this study shows the consistency of NO_3^- . Hence, we can assume that sources of NO_3^- could be from short range atmospheric circulation being dissimilar to the Antarctic ice core, whereas nitrate did not change with increasing distance from the coastal site to the central region of the Antarctic observations, but sulphur species (e.g., SO_4^{2-}) and sea salt concentration (e.g., NaCl) were decreased (*Minikin et al., 1998; Jaenicke et al., 1992; Gras, 1993*) (<http://www.pa.op.dlr.de/aerosol/troll/t-untent2-proj-background.html>). Thus, historical trends of levoglucosan, nitrate and sulfate, and Antarctica ice core observation suggest that historical trends (e.g., NO_3^- and SO_4^{2-}) could be controlled by seasonal cycles of phytoplankton productivity, sea ice coverage, photochemical oxidation and/or soil microbes (*Wagenbach et al., 1998b; Jones et al., 1999, 2000*) from adjacent parts of the APA. Hence we found different trends of nitrate than other ice core studies in the NH (e.g., Summit Greenland and Svalbard) and SH (e.g., South Pole). These evidences further suggest that the anthropogenic effect in the southern Alaskan region could be tiny since 1660s-1980s, compared to those other ice core studies in the SH and NH.

5.3.2. Historical Concentration Changes of NO_2^-

Several components contribute to NO_2^- emissions, i.e., fossil fuel combustion, fuel-fired power plants, industrial facilities, human activities, natural activities (e.g., biological production of nitrite in seawater) and biomass burning being the most important source of NO_2^- and or nitrogen dioxide (NO_2) (e.g., *Casadio et al., 1999; Zehner et al., 1999; Bruzzone et al., 2003*) in the NH which has been characterized by climate change periodicity. In addition, biomass burning evidences reported elsewhere (e.g., North America, South America, Australia, Africa, India, North east Asia-Siberia and China) (*Crutzen et al., 1979, 1985; Andreae et al., 1988; Crutzen and Andreae, 1990; Lobert et al., 1990; Qadri, 2001; Mahowald et al., 2005; In et al., 2007; Sundarambal et al., 2010; Kundu et al., 2010; Pavulari et al., 2011*). Nitrite (NO_2^-) show higher spikes in 1716 (3.16 ng/g), 1818 (2.21 ng/g), 1861 (2.48 ng/g), 1893 (1.88 ng/g), 1934 (1.60 ng/g), 1947 (1.93 ng/g), 1966 (1.73 ng/g), 1990 (2.47 ng/g), 1991 (3.65 ng/g), 2001 (3.22 ng/g), 2002 (2.37 ng/g), 2003 (2.74 ng/g), 2004 (2.72 ng/g), 2005 (2.60 ng/g), 2006 (2.67 ng/g) and 2007 (1.97 ng/g) than its background level (range:BDL-3.66, ave. 1.18 ± 0.97 ng/g-ice). These periods (Figure 2b) are similar to higher spikes of NH_4^+ (not shown in figure) suggesting a significant source of natural and human activities in the source regions (e.g., *Casadio et al., 1999; Zehner et al., 1999; Bruzzone et al., 2003*). Such types of source regions could be activated in the adjacent parts of the APA, Canadian and eastern Siberian regions.

It should be noted that, there is multidecadal periodicity of higher spikes for NO_2^- (e.g., around 1680s, 1720s, 1770s, 1820s, 1850s, 1890s, 1920s, 1940s, 1960s and 1990s) which suggests the long range atmospheric circulation was also significant, which can be

somewhat quantified by the Kamchatka ice core δD record from Northeast Asia (Figure 2b, g). This δD record in the Kamchatka ice core follows atmospheric transport from lower to higher latitudes in the North Pacific (e.g., Sato et al. 2014)⁷⁷. In addition, NO_2^- is gradually increasing after the 1920s suggesting that NO_2^- could be from a continental site and/or point source or local source of APA. It also further suggests that a major source could be changed from marine to continental and/or source strength could be changed (decreased) similar to δD record of the Kamchatka during the same periods (Figure 2g), which is also situated in the western North Pacific.

Hence, it also reveals that NO_2^- exhibits specific local to regional tropospheric transport behaviours in the North Pacific region (e.g., many ice core records do not show the significant concentration of nitrite). Moreover, it suggests that impact of anthropogenic pressure in southern Alaska is reflected significantly by NO_2^- after the 1920s compared to 1660s-1910s. Such types of anthropogenic pressure could be from industrial and biomass burning activities in eastern Siberia and adjacent parts of Alaska (Moore et al., 2006). For instance levoglucosan (preparing manuscript from same ice core) showed higher concentration in 1989, 1991, 1997, 1998, 1999, 2002 and 2004-2008. Thus, it can stipulate the transport and fate of NO_2^- impact before and after the 1920s and 1990s-2008 over the southern Alaskan region.

5.3.3. Historical Concentration Changes of SO_4^{2-}

Primary sources of sulfate (e.g., non sea salt SO_4^{2-}) are pyrite weathering, leaching-evaporation, agricultural activities-fertilizers, meteoric precipitation and dimethylsulfide (DMS) (Kaufmann *et al.*, 2010; Cortecchi *et al.*, 2002). In other words, it can be obtained from secondary and terrestrial sulphate sources, individual volcanic activities and the stratosphere (Kaufmann *et al.*, 2010). Total SO_4^{2-} (Figure 2e) shows few higher spike periods than its background level (range: BDL-168, ave. 32.9 ± 31.6 ng/g-ice). Figure 2d and 2e show somewhat uniformity of historical concentration trends for sea salt SO_4^{2-} (ss- SO_4^{2-}) and total SO_4^{2-} since 1660s-1980s (except in 1786, 1909 and 1913) and drastically higher spikes after the 1980s for some points. We estimated non-sea salt sulfate (nss- SO_4^{2-}), using a method reported by Kunwar and Kawamura, (2014), showing multidecadal trends being similar to NO_2^- , except for some points (Figure 2b, c). Non-sea salt sulphate (nss- SO_4^{2-}) trends are different (Figure 2c) than ss- SO_4^{2-} and total SO_4^{2-} .

Svalbard-Austfonna and Skobreen (Simoes and Zagorodnov, 2001), Svalbard-Snoeffjellaafonna (Goto-Azuma and Koerner, 2001), many sampling sites from coastal to the central part of Greenland (Legrand and Mayewski, 1997; Mayewski *et al.*, 1986) and a 100 year record of the Agassiz ice cap of Canadian Arctic Island (Koerner *et al.*, 1999) showed significant increasing historical trends since 1930s – 1990s, which were associated with anthropogenic activities in the source regions. Moreover, recent study of SO_4^{2-} records from the Lomonosovfonna-Svalbard ice core (ca. 800 year) showed increasing trends after an industrial revolution due to Eurasia and North America source regions (Moore *et al.* 2006; Kekonen *et al.*, 2005).

The above studies, trends of nss- SO_4^{2-} and total SO_4^{2-} (Figure 2c, e) suggest that total

SO₄²⁻ and/or non-sea salt SO₄²⁻ (nss-SO₄²⁻) could not be altered due to an industrial revolution in the NH before the 1980s. Hence, higher spikes of nss-SO₄²⁻ could be derived from other precursor compounds rather than industrial activities (*e.g.*, Kaufmann *et al.*, 2010; Cortecchi *et al.*, 2002). It has been suggested that nss-SO₄ and MSA⁻ are produced in the marine boundary layer (MBL) by photochemical oxidation of DMS, which is in turn an oxidation product of dimethyl-sulfoniopropionate (DMSP) emitted during biological activities (Kaufmann *et al.*, 2010; Legrand and Pasteur, 1998). Kaufmann *et al.* (2010) reported that many phytoplankton groups (*dinoflagellates* and *coccolithophorides*) and *Phaeocystis* produce DMSP during blooming periods (Legrand and Pasteur, 1998). Legrand and Pasteur (1982) confirmed that oxidation of DMS is always nss-SO₄²⁻ for an ice sheet. Thus, a major source of nss-SO₄²⁻ (including total SO₄²⁻) could be trapped/incorporated before and after snow deposition (Silvente and Legrand, 1993; Hansson, and Saltzman, 1993) from marine sources rather than continental sources.

These historical trends of SO₄²⁻, NO₂⁻, NO₃⁻ and MSA⁻ could be controlled by seasonal cycles of phytoplankton productivity, sea ice coverage, photochemical oxidation and/or soil microbes (Wagenbach *et al.*, 1998b; Jones *et al.*, 1999) from adjacent parts of the APA being similar to Antarctic observations, whereas sulphur species (*e.g.*, SO₄²⁻) and sea salt concentrations were decreased with increasing distance from the coast (Minikin *et al.*, 1998; Jaenicke *et al.*, 1992; Gras, 1993). Hence, Antarctica studies showed that seasonal cycles of sulphur species (*e.g.*, SO₄²⁻) were more pronounced with maximum concentration in the local summer season (Minikin *et al.*, 1998; Jaenicke *et al.*, 1992; Gras, 1993). (<http://www.pa.op.dlr.de/aerosol/troll/t-untent2-proj-background.html>).

Hence, changes of terrestrial sulfate concentration after an industrial revolution were not sufficient to show the increasing trends for an Alaskan glacier before the 1980s. Drastic changes of SO_4^{2-} , NO_2^- and NO_3^- after the 1980s are to be considered as climate change effect in the NH and/or anthropogenic effect (including biomass burning) could be important perhaps from East Asian regions and other adjacent parts of southern Alaska. For example, a 10 day backward trajectory since 1992-2002 showed that southern Alaska obtained different air masses from the North Pacific Regions, East Asia, Eastern Russia, Siberia, the Okhotsk and Bering Seas, higher latitudes of Alaskan regions, the Gulf of Alaska, Japan, Canada and the Arctic Ocean in the troposphere (>300 hPa) (Yasunari and Yamazaki, 2009).

Similarly, nss- SO_4^{2-} (Figure 2c) show higher spikes around 1708, 1716, 1786, 1818, 1861, 1898, 1909, 1913, 1991-1992, 1999, 2004 and 2007 than its background level (range: BDL-132, ave. 21.9 ± 33.3 ng/g-ice). Higher spikes of nss- SO_4^{2-} cycle since 1660s-1890s (except, 1880s) are comparable to MSA^- (Figure 2c, f). Similarly, higher spikes of nss- SO_4^{2-} and MSA^- show common periods after the 1890s (except for 1910s and 1930s) in 1898, 1947, 1966, 1989, 1990 and 2004. Similarly, NO_2^- and nss- SO_4^{2-} show common periods of sporadic peaks in 1716, 1786, 1818, 1861, 1893, 1947, 1966, 1987, 2004 and 2007 (Figure 2b, c). Interestingly, ss- SO_4^{2-} concentrations (range: 2.90, ave. 22.7 ± 10.7 ng/g-ice) and NO_3^- show steady concentration trends since 1660s-1980s (except, for a few points) and they have also common higher spike periods after the 1980s (e.g., 1989, 1991, 1994, 1999, 2004, 2006 and 2007) than their background level concentrations (Figure 2a and d). These comparison may suggest the similarity of air masses (e.g., air mass chemistry), similarity of solar radiation influence, a similarity

effect of snow accumulation rate (e.g., NO_3^- and ss-SO_4^{2-} could be independent with snowfall accumulation rate) and similarity of stratospheric fallout effect (*Lyons and Mayewski, 1983*) over the southern Alaskan region.

5.3.4. Comparison to Open Ocean Water and Ice Core Records of Nitrogen

Species

Duce et al. (2008) reported oxidized nitrogen species, i.e., NO_x (NO and NO_2) and NH_3^+ and/or reduced inorganic and organic nitrogen, which are increasing since the industrial revolution for open ocean water. Oceanic deposition of nitrogen species are to be expected more for open ocean water of the North Pacific Ocean by anthropogenic activities and atmospheric deposition resulting in significant eutrophication (e.g., nitrogen, phosphorus and trace elements like sulfur, potassium, calcium, and magnesium) in the North Pacific (*Duce et al., 2008*). For example, most of the oceanic deposition of nitrogen are natural sources before AD 2000 for open ocean water and only coastal regions are impacted significantly through eutrophication (*Duce et al., 2008*). Natural eutrophication is a slow-aging process for a body of water, thus the process could be sped up by human activities (*Art, 1993*).

Moreover, almost all ocean surface areas have been drastically affected by anthropogenic activities since 2000 from their background levels (*Duce et al., 2008*). But increment and/or deposition of nitrogen species are lesser in the North Pacific and Atlantic Ocean compared to Southeast Asia, Bay of Bengal, Arabian Sea and western Africa (*Duce et al., 2008*). This Aurora Peak study shows higher spikes of anions (e.g., NO_2^- , NO_3^-) and cations (e.g., NH_4^+ , Ca^{2+} , and K^+ ; not shown in figure) after AD 2000. It

can be considered as a form of pollution since 2000-2008 (only two points in the 1990s, i.e., 1991 and 1998) for this study. In contrast, south Greenland-Dye-3 (*Mayewski et al., 1990*), central Greenland-Summit (*Legrand and De Angelic, 1996*), Canadian low to high Arctic sites (*Koerner et al., 1999*), Lomonosovfonna-Svalbard (*Moree et al., 2006*), Antarctic Dome C (*Legrand and Delmas, 1988*) and the South Pole (*Mayewski and Legrand, 1990*) showed anthropogenic input earlier than Aurora Peak's glaciers. This suggests that the anthropogenic effect in the North Pacific region is slow compared to other sites. Hence, there is no nitrogen species (NO_2^- , NO_3^- and NH_4^+) deposition discrepancy between ice core records (this study) and open ocean water in the North Pacific.

This diversity of concentration trends of NO_3^- , ss-SO_4^{2-} and MSA between Aurora Peak and other ice core records reveals the sensitivity of the environment to perturbations. It is possibly related to coastal climatic perturbations in southeast Alaska. Sources of NO_x (e.g., NO_3^-) over the Alaskan glaciers are consistent since the 1660s–1980s which could be significantly controlled by different factors such as soil exhalation, biomass burning, lightning, galactic cosmic rays, stratospheric oxidation of N_2O , and ionospheric dissociation of N_2 rather than industrial activities in the NH (*Legrand and Mayewski, 1997*). For instance, soil exhalation was an important factor for concentration of NO_3^- in the Greenland ice core records (*Legrand and Mayewski, 1997*; *Legrand and Kirchner, 1990*); meanwhile, the stratosphere controlled some fraction of NO_3^- to the Antarctic regions (*Legrand and Mayewski, 1997*).

5.3.5. Comparison to Biomass Burning Tracer of Ice Core Records

Mount Logan, Yukon (Canada) showed high concentration of black carbon during 1800-1810, 1850-1950 and GISP2 showed gradual increase of insoluble micro particles in the 1850-1870s, 1885-1900, 1910-1920 which are discussed about “Pioneer Agriculture Revolution (PIAGREV), i.e., biomass burning in the source regions, e.g., Alaska and Siberia and increase in atmospheric turbidity i.e., “clear-cutting”, biomass burning and tilling of topsoil, respectively (*Holdsworth et al., 1996, references therein*). In addition, NH_4^+ , was increased at the central Greenland (GISP2), southern Greenland (20D) and Mount Logan, Yukon, Canada during this periods (*Holdsworth et al., 1996; Savarino and Legrand, 1998*).

We found significant concentrations of levoglucosan (biomass burning tracer, e.g., *Siomeit, 2002*) from the same ice core (e.g., *Pokhrel et al., 2014*). Only 10 out of 149 samples showed below detection limit (BDL) of this compound. This tracer (range: BDL-20801, average: 363 ± 1821 ng/L) showed significant concentrations in 1665 (198 ng/L), 1716 (990 ng/L), 1786 (7056 ng/L), 1818 (409 ng/L), 1913 (20,801 ng/L), 1947 (435 ng/L) and 1966 (692 ng/L) than its background level (except for 1665) are being almost similar to higher spikes of anions periods.

These common periods for higher spikes of anions (e.g., NO_2^- and nss-SO_4^{2-}) and cations (e.g., NH_4^+ ; not shown in Figure) showed that there are big contradictions of concentrations between levoglucosan and these anions. For instance, nss-SO_4^{2-} showed higher spike in 1909 (41.3 ng/g) rather than in 1913 (27.6 ng/g), meanwhile levoglucosan showed lower concentration in 1909 (79.2 ng/L) compared to the 1913 (20,801 ng/L). Similarly, we found weak correlations of levoglucosan with NO_2^- ($R = 0.17$), NO_3^-

(0.034), total SO_4^{2-} (0.15), nss- SO_4^{2-} (0.033), total K^+ (0.06), nss- K^+ (0.028), nss- Ca^{2+} (0.072) and NH_4^+ (0.09). These results suggest that biomass burning activities were not significant at all periods for higher spikes of these anions. It also further suggests that biogenic emission and other human activities could be significant during the 19th century rather than forest fires. In addition, historical trends of anions (sporadic peaks) suggest that source could be changed and/or controlled during 1900s (*Whitlow et al., 1994*). It should be noted that mid to late 1800s are to be considered to be the Little Ice Age (*Mayewski et al., 1993*). Recent increase of the concentration trends in the source regions can be considered as a climate driven (*Whitlow et al., 1994, reference therein*) including all types of human activities in the adjacent parts of the Aurora Peak.

Moreover, correlations of NH_4^+ with ss- K^+ ($R = 0.43$), nss- SO_4^{2-} (0.16) and nss- Ca^{2+} (0.14) are higher (even we do not find good correlations) compared to correlations of NH_4^+ with nss- K^+ (0.35), ss- SO_4^{2-} (0.12), ss- Ca^{2+} (0.12), and Na^+ (0.00). Correlations of NH_4^+ with NO_2^- ($R=0.94$) and NO_3^- (0.41) suggest that source of NH_4^+ and NO_2^- could be same. Hence, at least NO_2^- is most likely produced by the microbial oxidation of NH_4^+ coming from minerals dust (e.g., clay soils) into nitrite (*Amoroso et al., 2010*), which is associated with snow particles. Weak correlations between NH_4^+ with NO_3^- (0.41) and NO_3^- with NO_2^- (0.41) may also suggest that nitrite could not be oxidized to nitrate by nitrite-oxidizing bacteria (NOB) during nitrification (*Amoroso et al., 2010, references therein*) rather than other sources, which are discussed above.

5.3.6. Historical Concentration Changes of MSA⁻

Marine biological DMS produced sulfate and methanesulfonate acid (CH₃SO₃⁻). Methanesulfonate acid (MSA⁻) is the second generation oxidation product of DMS, and the source of MSA⁻ is only the DMS in the ocean and dependent upon the weather and/or climate (*Kaufmann et al., 2010; Legrand and Mayewski, 1997; Hansson, and Saltzman, 1993; Ivey et al., 1986; Saigne, and Legrand, 1987*). Higher concentrations of MSA⁻ (range: BDL-386, ave. 68.9 ± 88.2 ng/g-ice) during 1786 (104 ng/g), 1824 (95.9 ng/g), 1861 (95.2 ng/g), 1880 (203 ng/g), 1898 (135 ng/g), 1934 (116 ng/g), 1947 (99.4 ng/g), 1987 (107 ng/g), 1988 (327 ng/g), 1989 (204 ng/g), 1990 (386 ng/g), 1991 (204 ng/g), 1999 (155 ng/g), 2001 (278 ng/g), 2002 (334 ng/g), 2003 (109 ng/g) and 2004 (279 ng/g) can be attributed to increased biological productivity in the adjacent parts of Alaskan regions (Figure 2f). We found that the MSA⁻ trend is somewhat decreasing since the 1890s-1980s compared to the NO₂⁻ trend (Figure 2b, f), which is similar to global phytoplankton decline decades (*Boyce et al., 2010*). In the same ways, we can explain higher concentrations of these compounds since the 1660s-1910s. The complex mechanism of thermohaline circulation and productivity of marine biota are very complex, and reported elsewhere (*Boyce et al., 2010; references therein*). Hence, spikes of MSA is emitted from the ocean during biologically more active years and/or decades which could be associated with also thermohaline circulation (*Boyce et al., 2010; references therein*) in the Northern Pacific regions. Interestingly, periods of higher MSA (except, for few point, e.g., 1880) are similar to SO₄²⁻ (e.g., nss-SO₄²⁻ and/or total SO₄²⁻) suggesting the importance of transformation, transport and depositional processes but this doesn't necessarily infer a common source region for these species (*Hansson and*

Saltzman, 1993).

DMS could be injected into the atmosphere and oxidized to nss-SO_4^{2-} as well as MSA^- in the MBL (Kaufmann et al., 2010; *Legrand and Mayewski, 1997; Vandal et al., 1993; Legrand et al., 1992*). Particularly, MSA^- and nss-SO_4^{2-} have similar historical trends since the 1660s-1890s (Figure 2c, f) suggesting that the major source could be DMS from the marine atmosphere. Moreover, the variability (ratios) in the $\text{nss-SO}_4^{2-}/\text{Na}^+$ (Figure 3a) indicates the variability of sulfate from sources other than sea spray salt. The covariability in the temporal trend with MSA^-/Na^+ (Figure 3b) suggests its formation from the oxidation of BVOCs emitted from the ocean surface in the marine atmosphere. Thus similar temporal trends observed by MSA^-/Na and $\text{nss-SO}_4^{2-}/\text{Na}^+$ (Figure 3a, b) suggest their formation from DMS oxidation.

This relation between SO_4^{2-} and MSA^- further supports that SO_4^{2-} and MSA^- could be coupled with past climate change in the Pacific region, which somewhat follows the δD recorded at Kamchatka (Figure 2g). In contrast, MSA^- and SO_4^{2-} (Figure 2c, d, e, f) have little discrepancy for some higher spikes (e.g., 1909-1913) suggesting the non-biogenic sulfur sources (e.g., gypsum emission from desert) could be activated (*Legrand and Mayewski, 1997*) and/or changing the source strength and independent sources of sulfur (*Hansson and Saltzman, 1993*) via long range atmospheric transport. For example, the eastern Greenland-Renland deep ice core showed such a discrepancy between MSA^- and SO_4^{2-} , and MSA^- records of Vostok (*Hansson and Saltzman, 1993*), respectively. Thus, discrepancies between the historical concentration trends of SO_4^{2-} and MSA^- during the 19th century could be associated with shifting the principle source regions in the polar precipitation (*Hansson and Saltzman, 1993; Legrand and Delmas, 1988*).

5.4. Responses of Alaskan Ice Core to Climate Change

We detected significant concentrations of low molecular weight fatty acids (LFAs) ($C_{14:0}$, $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$), which are strongly associated with marine biogenic sources (Pokhrel *et al.*, 2014). Interestingly, these LFAs are strongly associated with multi-decadal climate periodicity e.g., Pacific Decadal Oscillation (PDO), North Pacific Gyre Oscillation (NPGO) and Arctic Oscillations (AO) (Pokhrel *et al.*, 2015). We found very weak correlations (<0.19) of these fatty acids ($C_{14:0}$, $C_{16:0}$, $C_{17:0}$, $C_{18:0}$ and $C_{18:1}$) with NO_2^- and NO_3^- suggest that NO_2^- and NO_3^- could be from continental sources rather than marine. Similarly, correlation between methanesulfonate (MSA^-) and LFAs (> 0.70) suggest the marine biogenic emission. Relations between MSA^- with $nss-SO_4^{2-}$ ($R=0.85$), MSA^- (except for 1907, 1998 & 2005) with Cl^- (0.71), MSA^- (except for, 1915, 1990 & 2001) with F^- (0.81), MSA^- (except for 8 points, e.g., 1990 and 2005) with NO_3^- (0.64) and MSA^- with LFAs (e.g., $C_{14:0}$, $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$) are positive (0.71, 0.79, 0.81 and 0.88, respectively). Moreover, we found good correlation of Na^+ (except for, 1988, 1989 & 1999) with MSA^- (0.71) and Na^+ with $nss-SO_4^{2-}$ (0.84). These results also further support that MSA^- , $nss-SO_4^{2-}$ and Cl^- , F^- and somewhat NO_3^- are associated with marine atmosphere suggest that Alaskan anions (e.g., MSA^- , $nss-SO_4^{2-}$, F^- and Cl^-) are controlled by climate periodicity cycle (Pokhrel *et al.*, 2015).

5.5. Conclusions

This study has disclosed a new insight for glaciochemistry time series that spans the last 343 years. We detected interesting historical geochemical cycles of anions i.e., nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-}) and methanesulfonate ($CH_3SO_3^-$) from 1665-2008,

which are completely different than other ice core records in the Northern and Southern Hemispheres. NO_3^- and sea salt SO_4^{2-} showed consistency in historical trends since the 1660s-1980s. CH_3SO_3^- and nss- SO_4^{2-} cycles are similar since the 1660s-1890s. Common periods of spike for all anions (except for some points) suggest that these anions could be attributed from their same source regions, similarity of air mass chemistry, and similar effect of snowfall accumulation rate. These results further suggest that Alaskan anions could be associated with the pristine glaciochemistry rather than the contaminated atmospheric transport from the East Asian regions. In contrast, significant impacts from human activities are recorded and concentrations are drastically increased from its background level since the 1990s, which are somewhat similar to the open ocean water of the North Pacific. Hence, this study suggests that the industrial revolution's impact is minimal in the northern North Pacific region before the 1990s.

Kamchatka ice core δD periodicity is similar to anions periodicity (except few points, e.g., 1820s and 1880s), which can further demonstrate that the North Pacific paleoclimate information is imprinted in the ice core from Alaska. Hence, multi-decadal scale atmospheric transport from middle to higher latitudes in the North Pacific is reflected as periodic cycles of NO_2^- , SO_4^{2-} and CH_3SO_3^- , which could be associated with climate oscillations, and are to be controlled as well. This agreement further suggests that Arctic Oscillation (AO), Pacific Decadal Oscillation (PDO) and/or North Pacific Gyre Oscillation (NPGO) may influence the anions periodicity cycles, which can somewhat, alter the concept of other ice core studies in the Northern and Southern Hemispheres corresponding to the anthropogenic activities.

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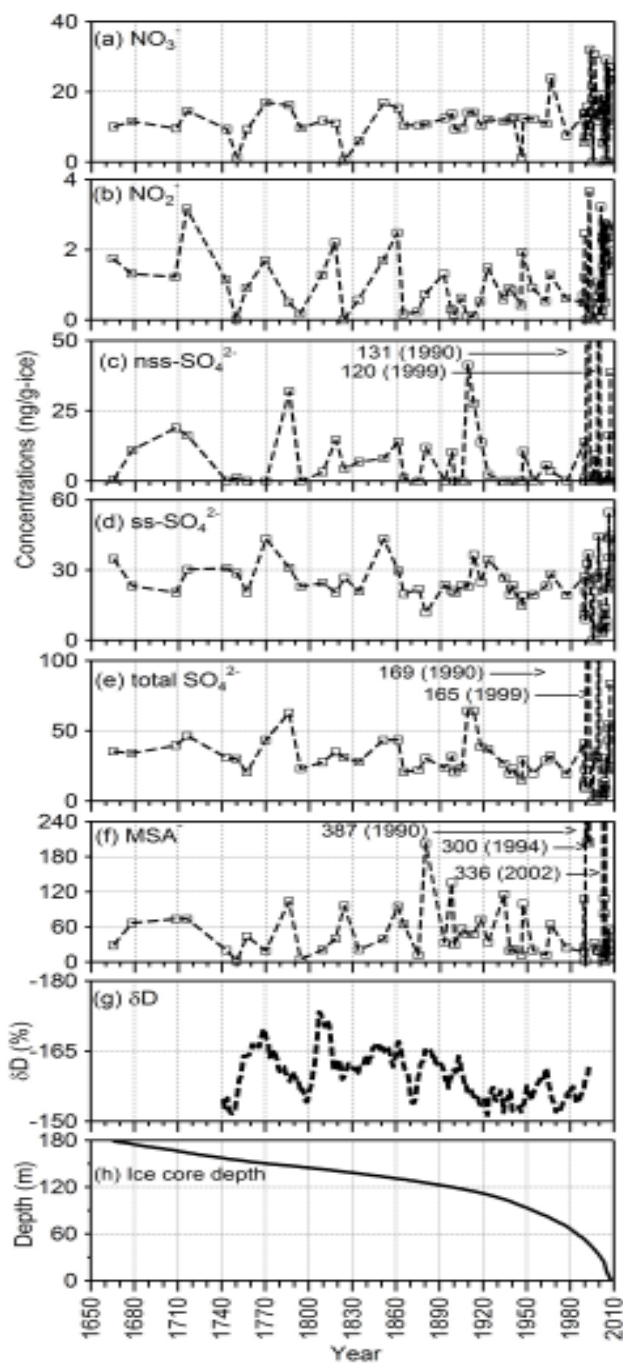


Figure 2. Historical changes of selected anions (a) – (f) in the ice core collected from Aurora Peak in southern Alaska and (g) 20 year running mean (20RM) of snowfall accumulation rate of hydrogen isotope ratio (δD) profile from Kamchatka Peninsula, Russia (Sato *et al.*, 2014).

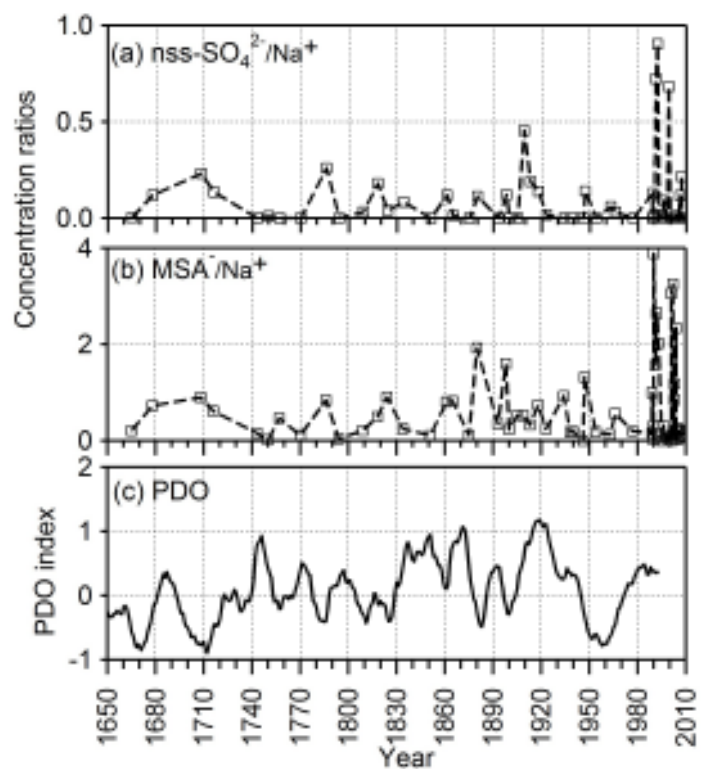


Figure 3. Historical changes of ratios (a) MSA^-/Na^+ and (b) $\text{nss-SO}_4^{2-}/\text{Na}^+$ since 1734-2008 in the ice core collected from Aurora Peak in southern Alaska.

Chapter 6. Ice core records of biogenic secondary organic tracers from isoprene and monoterpenes from Aurora Peak in Alaska since the 1660s

6.1. Introduction

Terrestrial and marine atmospheric vegetations produce huge amount of biogenic volatile organic compounds (BVOCs), isoprene, monoterpenes, sesquiterpenes and oxygenated hydrocarbons, and anthropogenic volatile organic compounds (VOCs) are released from many types of human activities (*Guenther et al., 2006; Fu et al., 2009, references therein*). BVOCs and/or VOCs are oxidized to secondary organic aerosol (SOA) by the oxidation of gas-phase precursors in the atmosphere (*Fu et al., 2010a; Celia et al., 2015*) suggesting that SOA can be formed from the VOCs, either in the gas or aqueous phase, making less volatile products. Kanakidou et al., 2005 reported that primary organic aerosol (POA) and SOA control the physicochemical properties of atmosphere and SOA are ubiquitous in the atmosphere (*Fu et al., 2009; Kunwar and Kawamura 2014a; Myriokefalitakis et al., 2011; Quinn et al., 2014;*). Moreover, physical, chemical, and biological processes of organic and inorganic aerosols are involved and alter the geochemical cycles (e.g., biogeochemical cycles) in the Northern Hemisphere (NH) (*Celia et al., 2015; Kawamura et al., 2001; Quinn and Bates, 2014; Seki et al., 2012; Kunwar and Kawamura, 2014b; Pokhrel et al., 2015*).

McNeill et al. (2012) reported that organic compounds in snow-glaciers and/or in ice particles could be biological in origin, deposited from aerosols or atmospheric gases as well as chemically. Aerosol samples have showed both sources for these compounds and

reported elsewhere. For instance, terpenes are released from vegetation, together with aromatic hydrocarbons from anthropogenic sources as precursors of SOA (*Hu et al., 2008; references therein*). There are many studies of monoterpene and isoprene SOA tracers for aerosol samples for short-term duration, which are reported elsewhere (*Fu et al., 2013; Hu et al., 2008, references therein*). Pinonic acid, pinic acid and 3-hydroxyglutaric acids are reported to better understand changes of monoterpene secondary organic tracers. Similarly, isoprene SOA tracers, e.g., 2-methylglyceric acid, cis 2-methyl 1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, 2-methylthreitol and 2-methylerythritol are also reported from same ice core samples.

This study demonstrates the historical trends of SOA tracers that are derived from atmospheric photo oxidation of isoprene and α/β - pinene oxidation products (i.e., monoterpenes and isoprene) in the source regions of Aurora Peak, southern Alaska. It also reveals the biological source strength of these tracers before and after industrial revolution in the NH. Here, first time, we report these tracers from mountain glaciers. Hence, it will be more worthy to better understand both POA and SOA in the Northern North Pacific regions since the 1660s.

6.2. Samples and Analytical Procedures

6.2.1. Site Description

Japanese ice core group drilled 180 m long (ca. 274 years) ice core in the saddle of the Aurora Peak of Alaska in 2008 AD, which is located southeast of Fairbanks (63.52°N; 146.54°W, elevation: 2,825 m). Samples were directly transported to the

Institute of Low Temperature Science (ILTs), Hokkaido University, Japan. The ice core ages were determined by annual counting of hydrogen isotopes (δD) and Na^+ seasonal cycles and age control was provided by reference horizons of tritium peaks in 1963 and 1964. By this methods, bottom of sample was estimated to be 343 years old; i.e., 1665 AD [*Tshushima, 2011; Tsushima et al., 2014*]. The 180 m long ice core sample was cut into ~50 cm long pieces and transported to the laboratory of the Institute of Low Temperature Science (ILTS), Hokkaido, University, Japan and stored in a dark cold room at -20°C until analysis.

6.2.2. Chemical Analysis

Ice core were derivatized with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride (TMCS) and pyridine and peaks were analyzed by using GC mass and GC/MS system, which is reported elsewhere (e.g., *Fu et al., 2013, 2010*). Pinonic acid, pinic acid and 3-hydroxyglutaric acids are analyzed as monoterpene secondary organic tracers. Similarly, isoprene SOA tracers, e.g., 2-methylglyceric acid, cis 2-methyl 1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, 2-methylthreitol and 2-methylerythritol are also detected by using GC mass and GC/MS system. Recovery test were performed as real ice core sample by using authentic standards. Results were satisfactory (e.g. more than 80%) to analyze real ice samples. Triplicate analysis was also conducted. Analytical errors were less than 8%. Similarly, laboratory blank was less than 5% of real ice core samples. All the data are reported here were corrected for this laboratory blank.

6.3. Results and Discussion

6.3.1. Historical Concentrations of Monoterpene Tracers

Table 1 showed significant concentrations of monoterpene (e.g., pinonic, pinic and 3-hydroxyglutaric acid) and isoprene SOA tracers (e.g., 2-methylglyceric acid, cis 2-methyl 1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, 2-methylthreitol and 2-methylerythritol) since the 1660s from southern Alaska. Pinic acid (average, 131 ± 174 ng/L) showed higher spikes in 1750-1840s, 1870s, 1910, 1919, 1927, 1934, 1970, 1987, 1991, 1997-2000, 2004-2008 which is similar to historical trend of pinonic acid (ave. 44.9 ± 69.5 ng/L) except for 1980s (Figure 3a,b). These periods can be considered as significant monoterpene oxidation periods corresponding to the formation of SOA in the North Pacific region since the 1660s. Pinonic and pinic acids are detected as α/β -pinene oxidation productions. These acids were observed in smog chamber experiments (*Glasius et al., 2000*), which can be produced from photooxidation of α/β -pinene via reactions with O_3 and OH radicals (*Hoffman et al., 1997; Zhang et al., 2004; Hallquist et al., 2009; Fu et al., 2010*).

Interestingly, pinic acid (131 ng/L) is near about three times higher than pinonic acid (44.9 ng/L), which contradicts the aerosol study of Mt. Tai in central east China and tropical India (*Fu et al., 2010a, 2010c*). It should be noted that vapor pressure of pinonic acid is near about two times higher than pinic acid (*Fu et al., 2010c*). In addition, similar pattern can be observed in other aerosol studies in the Northern Hemisphere, e.g., central Greece (*Kavouras et al., 1999*), Sierra Nevada Mountains of California (*Cahill et al., 2006*) and North Carolina (*Bhat et al., 2007*). Source regions could be different for Alaskan regions compared to these aerosol samples study (e.g., Mt. Tai) indicating the

coniferous forest, which is likely possible for southern Alaskan regions and it is similar to aerosol sample studies of Research Triangle Park, USA and Germany (e.g., *Kleindienst et al.*, 2007; *Plewka et al.*, 2006). The correlation between pinonic acid and pinic acid ($R = 0.78$) indicates similar source regions and similar formation pathways and/or atmospheric fate for southern Alaskan regions since the 1660s (Figure 4a).

We detected significant concentrations of 3-hydroxyglutaric acid (3-HGA) showed completely different historical trends than pinic and pinonic acids. It showed sporadic peaks in 1773, 1785, 1809-1845, 1871-1875, 1910-1915, 1930, 1934, 1947, 1991, 1994, 1997, 1999, 2004, 2005 and 2008 than its background level (ave. 28.4 ± 145 ng/L) since the 1660s (Figure 3c). This compound was also generated in smog chamber of α -pinene with an irradiation of UV in the presence of NO_x (Clayes et al., 2007). It should be noted that we didn't detect β -caryophyllinic acid and other related compounds since the 1660s suggest the source regions of BVOCs. Many aerosols sample showed higher concentrations during late winter (e.g., Fu et al., 2010b; reference therein). These results suggest insignificant BVOCs for this sampling site further reveals insignificant ozonolysis and/or photo-oxidation product of β -caryophyllene production (*Jaoui et al.*, 2007) in the source regions of southern Alaska. Moreover, correlation between pinic acid and 3-HGA ($R = 0.52$) pinonic acid and 3-HGA (0.41) are somewhat poor compared to correlation between pinic acid and pinonic acid (0.78) indicates different source regions and different formation pathways and/or atmospheric fate for historical trend of 3-HGA over the southern Alaskan regions since the 1660s (Figure 4a,b,c).

Interestingly concentrations trends of these three compounds are somewhat decreased after 1920s (except, for 1934, 1938 and 1973) and some sporadic peaks during the 1990s

suggest that source could be shifted for this sampling site. It should be noted that global scale contribution of BVOCs to SOA is greater than that of anthropogenic VOCs (*Fu et al., 2010b, references therein*). BVOCs can be derived from vegetations (e.g., isoprene, monoterpenes, sesquiterpenes) as well as alcohols, aldehydes and ketones, i.e., oxygenated hydrocarbons (*Guenther et al., 2006*).

Pinic and pinonic acids also showed somewhat similar historical trends with 2-methylglyceric (Figure 3a) at least before the 1980s and they have good correlations ($R = 0.70$ and 0.83) during these periods and somewhat poor correlation of 3-HGA with 2-methylglyceric (0.57) compared to pinic and pinonic acids. Similarly, these compounds have similar historical trends with 2-methylthreitol and 2-methylerythritol (Figure 2a, b, and 3b, c) since the 1660s to 2008. Relations between pinic and pinonic with 2-methylthreitol are 0.78 , 0.77 , respectively (Figure 4a, b). In addition, correlations between pinic and pinonic with 2-methylerythritol are 0.71 and 0.75 , respectively (Figure 4d, e). In contrast, correlations of 3-HGA with 2-methylthreitol and 2-methylerythritol are 0.49 and 0.27 , respectively (Figure 4c and 4f).

It should be noted that historical trends are similar to each other for pinic and pinonic acids and correlation between them is 0.78 suggest the same source regions and/or same formation pathways could be activated compared to 3-HGA monoterpene SOA tracer and other isoprene BVOCs tracers (e.g., Figure 3d,e and f). For instance, correlations (R) of pinonic and pinic acid with 3-methyl-2,3,4-trihydroxy-1-butene are 0.51 and 0.63 , and correlations with cis 2-methyl 1,3,4-trihydroxy-1butene are 0.49 and 0.52 , respectively, before the 1980s. Concentration of 3-HGA is 4^{th} times lower than pinic and comparable to pinonic acid suggest the source strength of these compounds for biogenic SOA tracers

(Figure 3a-c) before and after industrial revolution and contribution of BVOCs to SOA tracers rather than anthropogenic VOCs in the source regions for southern Alaska.

6.3.2. Historical concentrations of isoprene SOA tracers

We detected six isoprene tracers (e.g., 2-methylglyceric acid, cis 2-methyl 1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, 2-methylthreitol and 2-methylerythritol), which are more active with oxidants agents (e.g., OH, O₃ and NO₃) and their oxidation products in particle phase, they can lead to secondary organic aerosol (SOA) formation (*Atkinson and Arey, 1998; Guenther, et al., 2006; Fu et al., 2010*) from the photooxidation of both anthropogenic and biogenic volatile organic compounds (VOCs) (*Hoffmann et al., 1997; Zhang et al., 2004; Kanakidou et al., 2005; Sato, 2008; Fu et al., 2010*). The sources of VOCs are isoprene, monoterpenes, sesquiterpenes, and oxygenated hydrocarbons such as alcohols, aldehydes and ketones (*Hoffmann et al., 1997; Zhang et al., 2004; Kanakidou et al., 2005; Guenther et al., 2006; Sato, 2008; Fu et al., 2010; references therein*).

2-methylglyceric acids can be formed from oxidation of methacrolein and methacrylic acid from two major gas-phase oxidation products of isoprene (*Surrat et al., 2007; Hu et al., 2008*), which can be associated with land sea breeze atmospheric circulation (*Claeys et al., 2004; Fu et al., 2010b, references therein*). It showed higher concentrations in 1684 (49.4), 1692 (46.9), 1698 (60.1), 1750 (74.8), 1786 (175), 1794 (42.6), 1802 (50.7), 1809 (43.2), 1818 (60.1), 1824 (40.1), 1865 (51.9), 1870 (83.4), 1875 (93.1), 1880 (73.1), 1898 (44.3), 1913 (166), 1947 (51.9), 1954 (57.2), 1973 (144), 1977 (67.3), 1993 (230), 1998 (65.9), 1999 (71.8), 2004 (45.6), 2005 (282) and 2006 (49.2)

ng/L, respectively, than its background level (ave. 35.6, ± 47.6 ng/L) since the 1660s (Figure 3a). 2-methylthreitol showed higher spikes during 1665-1684, 1692-1708, 1720, 1728-1750, 1778-1818, 1865-1880, 1898, 1923, 1947, 1966, 1973 and 1993 than its background level concentration (ave. 349 ± 382 ng/L-ice), which are similar to 2-methylerythritol, except for 1720, 1757, 1764, 1840 and 2005 than its background level (692 ± 709 ng/L-ice) since the 1660s (Figure 3b and 3c). In contrast, cis 2-methyl 1,3,4-trihydroxy-1-butene showed higher concentrations in 1732, 1738, 1947, 1954, 1973, 1989, 1996-2001 and 2004-2007 than its background level concentration (ave. 23.1 ± 52.2 ng/L-ice) since the 1660s (Figure 3d). In addition, 3-methyl-2,3,4-trihydroxy-1-butene showed higher concentration in 1728, 1738, 1786, 1973, 1989, 1993, 1996-2000 and 2004-2006 than its background level (ave. 6.99 ± 17.1 ng/L-ice) since the 1660s (Figure 3e). Similarly, trans-2-methyl-1,3,4-trihydroxy-1-butene showed higher spikes in 1923, 1940, 1947, 1973, 1981, 1989, 1993, 1996-1999 and 2004-2007 than its background level concentration (ave. 36.4 ± 97.9 ng/L-ice) since the 1660s (Figure 3f).

These results suggest that isoprene products were significant in the source regions of southern Alaska during these periods. It also reveals that historical trends of isoprene products are somewhat similar with each other suggest that they are controlled by similar meteorological factors in the Northern North Pacific regions. Moreover, correlations of 2-methylglyceric acid with 2-methylthreitol, 2-methylerythritol, trans-2-methyl-1,3,4-trihydroxy-1-butene, cis 2-methyl 1,3,4-trihydroxy-1-butene and 3-methyl-2,3,4-trihydroxy-1-butene are 0.82, 0.67, 0.77, 0.75 and 0.83 respectively. Similarly, relations of 2-methylthreitol with 2-methylerythritol, trans-2-methyl-1,3,4-trihydroxy-1-butene, cis 2-methyl 1,3,4-trihydroxy-1-butene and 3-methyl-2,3,4-trihydroxy-1-butene are positive (

0.87, 0.57, 0.54 and 0.65, respectively). In addition, correlations of 2-methylerythritol with these tracers also showed positive (not shown in Figure).

These above all results suggest that atmospheric fate could be admired strongly by local or regional meteorological conditions and/or the absence of anthropogenic activities (e.g., influence of human activities). The most prevalent SOA precursors on a global scale are terpenoid compounds, which are emitted from plants and vegetations. It should be noted that, more than 100 organic compounds including many SOA precursors compounds are emitted from leaf litter and/or soil, which is insignificant compared to emission from plant and vegetations (*Celia et al., 2015; references therein*). In contrast, SOA formation in forest environment, i.e., from leaf litter and/or forest soil is also important, at least during spring and fall season compared to summer seasons (*Celia et al., 2015*). For instance, particle formation rate was high during spring season to soil and leaf litter of a boreal forest in southern Finland (*Makela et al., 2000; Bigg et al., 2004*). In addition, SOA precursors, terpenoids were high during late spring and autumn for boreal pine forest floor (*Aaltonen et al., 2011; Isidorov et al., 2010*). These result further suggest the sources and seasons of higher spikes during these periods for an ice core of Aurora Peak

6.4. Response of Ice Core Monoterpene and isoprene SOA Tracers and Lower Tropospheric Temperature

Wilson et al. (2007) reported that extra tropical Northern Hemispheric temperature departure (ENHT) has positive correlations with more than 25 different tree ring proxy records of the world, e.g., European Alps ($R=0.67$), western Siberia (0.61), Mongolia

(0.70), Nepal (0.49), Northern Yukon (0.60), Wrangell Mountains (0.60), British Columbia (0.77), Idaho (0.41) and Northern Quebec (0.42) (*Wilson et al., 2007, references therein*). Three isoprene tracers showed positive correlation with ENHT. Particularly, correlations between 5 points running mean (5-RM) of cis 2-methyl 1,3,4-trihydroxy-1-butene, 5-RM of 3-methyl-2,3,4-trihydroxy-1-butene, 5-RM of trans-2-methyl-1,3,4-trihydroxy-1-butene are 0.80, 0.73, 0.78, respectively. It should be noted that these compounds have weak correlations with other isoprene tracers and monoterpene tracers. Hence, these results suggest that these compounds are strongly associated with ENHT. It also reveals that these compounds have own sources compared to other monoterpene and isoprene tracers. But we can't mention any terrestrial and/or marine sources of these compounds by using these relations at this moment. We got increasing trends of three compounds (i.e., cis 2-methyl 1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene) since 1920s (except for few points), which are dissimilar to phytoplankton decline century of the North Pacific Ocean (e.g., *Boyce et al., 2010*).

We found 7-RM of ENHT have anticorrelations with 7-RM of 2-methylthreitol (0.47), and 7-RM of 2-methylerythritol (0.60). It should be noted that these isoprene SOA tracers (i.e., 2-methylthreitol and 2-methylerythritol) showed good correlations with monoterpene tracers (e.g., pinonic and pinic acid) as we have mentioned above. In addition, monoterpene tracers (i.e., pinonic, pinic and 3-HGA) also showed anticorrelations with ENHT. For instance, anticorrelation of 7-RM of ENHT with 7-RM of pinonic acid is 0.68 since the 1750s.

We got lower concentrations of pinonic, pinic, 2-methylglyceric, 2-methylthreitol and

2-methylerythritol (except for 1970s) since 1920s compared to rest of the years which is somewhat similar to phytoplankton decline century of the North Pacific (Boyce *et al.*, 2010). In the same ways, we can explain higher concentrations of these compounds since the 1660s-1910s. The complex mechanism of thermohaline circulation and productivity of marine biota are very complex, and reported elsewhere (Boyce *et al.*, 2010; *references therein*). Hence, these compounds (isoprene and monoterpene) are somewhat emitted from the ocean during biologically active years and/or decades which could be associated with also thermohaline circulation activities (Boyce *et al.*, 2010; *references therein*) in the Northern Pacific regions.

Reconstruction of coastal surface air temperatures (T) from Gulf of Alaska (GOA) using tree ring shows sharp decrease historical trends of June to September since 1800-1875 except around 1830s (e.g., Wilson *et al.*, 2007a), which is at least similar to lower concentrations of pinonic, pinic, 2-methylglyceric, 2-methylthreitol and 2-methylerythritol (Figure 1a-b and Figure 2a-c). It should be noted that sampling sites of this GOA temperature were located along the GOA, well to the south of the Brooks Range at about 68°N. This GOA temperature expresses a strong consistency with multi-decadal climate oscillation and short-term atmospheric activities (e.g., ENSO/El-Nino and/or Aleutian Low).

Lower concentration of these compounds during this period is further supported by historical trend of ENHT (Wilson *et al.*, 2007b). Decreasing trends of all these monoterpene and isoprene SOA tracers showed positive correlations with decreasing historical trends of ENHT during 1800-1860. Particularly, correlations (R) of each 11 points running mean (11-RM) of pinonic, pinic and 3-HGA with 11-RM of ENHT are 0.84, 0.86 and 0.54, respectively. Similarly, correlations of each 11-RM of all isoprene SOA tracers, e.g., Figure 2 (a - t) with 11-RM of ENHT are 0.84, 0.95, 0.94, 0.89, 0.82

and 0.67, respectively.

It should be noted that NH temperature departure and reconstructed solar irradiance are well correlated with many climate periodicity and non-periodicity cycles in the NH, which are reported elsewhere (*Wang et al., 2012; Rodionov, et al., 2007; Hartman and Wendler, 2005; Lean et al., 2005; Lean, 2000; Harvey and Hitchmann, 1996, Mantua et al., 1997; Trenberth and Hurrell, 1994;*). For example, Aleutian Low (AL) can easily alter the air mass flow position and intensity changes on the east and the west sides of its center, which can directly alter the heat exchange between Arctic region and the mid-latitude over the North Pacific regions (*Wang et al., 2012; Rodionov et al., 2007*), which suggest the meridional air mass circulation. Mantua et al. (1997) pointed out that the AL was significantly correlated with the Pacific Decadal Oscillation (PDO). For instance, the warm phase of PDO corresponds to the strong AL, while the cold phase of PDO corresponds to the weak AL. AL would have mixed continental and marine air mass, and more drive prevailing winds from northwestern Pacific regions to northeastward in the North America, which can intensify the positive North Pacific Index (PNI) over American west (*Trouet and Taylor, 2009*) can represent the 30°N-65°N, 160°E-140°W for decadal variations in the atmospheric circulation (<https://climatedataguide.ucar.edu>). Moreover, on a decadal scale, the AL has been consistently strong and has drifted eastward since the 1970s (*Wang et al, 2012*). These compounds also showed lower concentrations compared to previous decades, except for few points, e, g., Figure 1(a, b) and Figure 2(a-c) suggest continental sources for these compounds.

In contrast, Figure 2(d-e) showed positive correlations with ENHT since 1750s suggest that these three compounds are somewhat associated with marine atmosphere

and/or lower latitude atmospheric transport compared to other compounds. Using North Pacific Index (PNI) data can see these climatic oscillations effect. For instance, relations between 7-RM for each tracers, cis 2-methyl 1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene with 7-RM of NPI since 1899-2007 have anti but weak correlations ($R = 0.32, 0.31$ and 0.29 , respectively). Similarly, other compounds also showed weak correlations with NPI. These results strongly suggest that interactions with other atmospheric activities such as AL and/or El Niño/Southern Oscillation (ENSO), other decadal variability (or, atmospheric stability) are also important for these compounds.

This result further supported by Janout et al. (2013) from air-sea and oceanic heat fluxes of the northern Gulf of Alaska. Net heat flux and/or heat flux anomalies in winter are significantly increased during 1975-2010 (except around 1998) compared to 1950-1975 (Janout et al., 2013), which is similar to historical trends of cis 2-methyl 1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene (Figure 2d-f) suggest that concentrations of these compounds are controlled by temperature, pressure and wind field of GOA and/or Northern North Pacific regions. These three fields automatically alter the atmospheric transport (e.g., AL can alter the atmospheric transport), which are correlated with ENHT elsewhere (*Wilson et al., 2007a; Wang et al., 2012; Rodionov et al., 2007, references therein*) and it is likely for this sampling site.

6.5. Conclusions

These are tracers of monoterpene (e.g., pinonic, pinic and 3-hydroxyglutaric acids) and isoprene secondary organic aerosols-SOA (e.g., 2-methylglyceric, 2-methylthreitol and 2-methylerythritol, cis 2-methyl 1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene), which are derived from continental source regions rather than marine atmosphere.

Correlations of three compounds (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) with monoterpene tracers and other SOA tracers are weak. In contrast, correlation of monoterpene tracers and other SOA tracers (e.g., 2-methylglyceric acid, 2-methylthreitol and 2-methylerythritol) are strong. These correlation results suggest different source and shared transport, same source regions and shared transport, respectively.

In addition, net heat flux and/or heat flux anomalies in winter are significantly increased during 1975-2010 (except around 1998) compared to 1950-1975, which is similar to historical trends of 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. They showed lower concentrations during 1800-1860, which are similar to Gulf of Alaska (GOA) temperature and extra-tropical Northern Hemisphere temperature departure suggest that climate oscillations alter concentrations trends of monoterpene, and isoprene SOA tracers. Hence, increased and/or decreased biogenic emission capacity, source regions and/or atmospheric transport are changed significantly and could be associated with multi-decadal climate oscillations.

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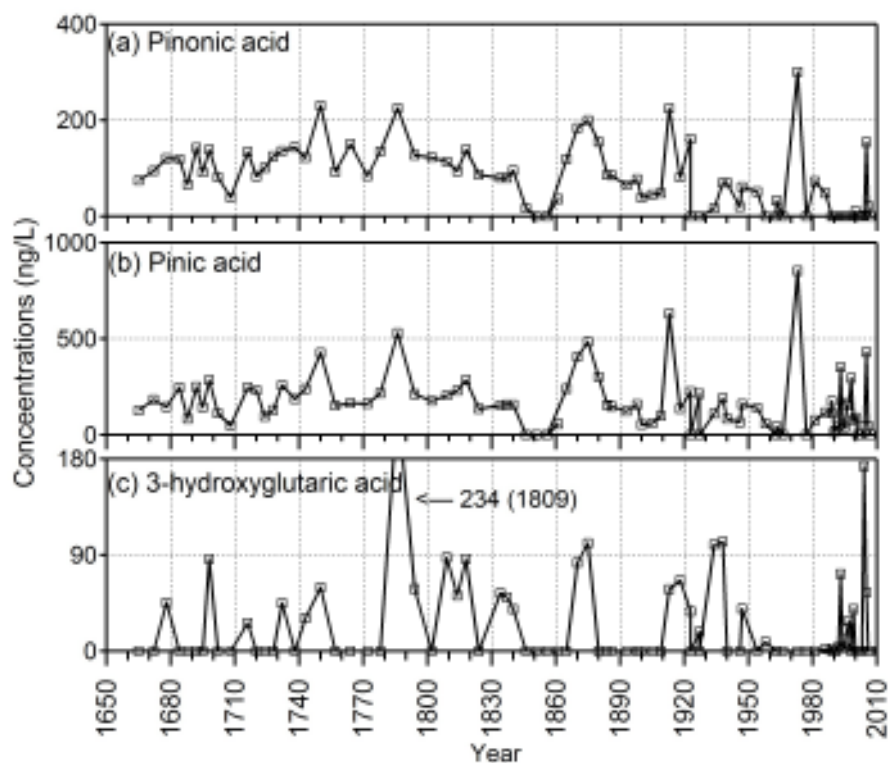


Figure 1. Concentration changes of (a) Pinonic acid, (b) Pinic acid (c) 3-hydroxyglutaric acid in the Alaska ice core records collected from Aurora peak.

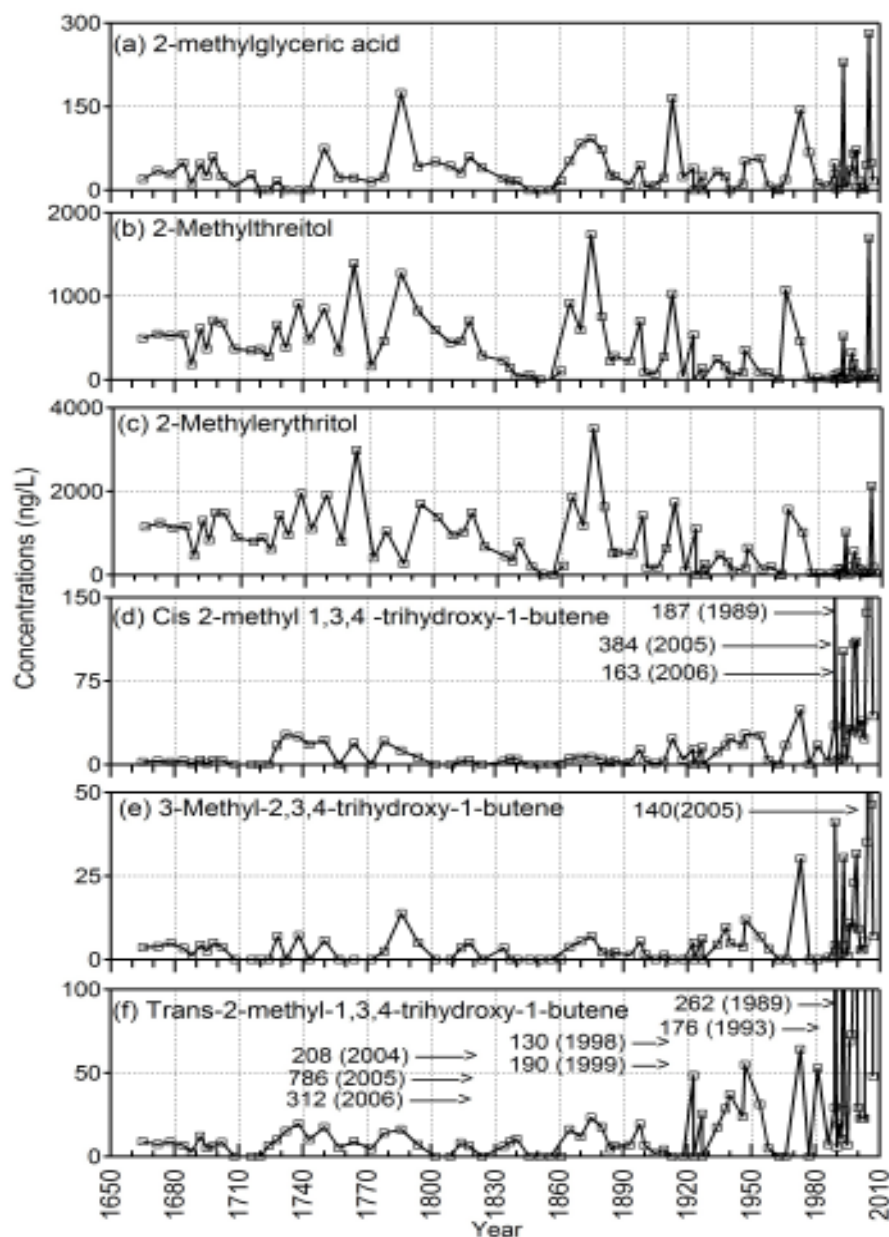


Figure 2. Concentration changes of (a) 2-methylglyceric acid, (b) 2-methylthreitol, (c) 2-methylerythritol, (d) cis 2-methyl 1,3,4-trihydroxy-1-butene, (e) 3-methyl-2,3,4-trihydroxy-1-butene and (f) trans-2-methyl-1,3,4-trihydroxy-1-butene in the Alaska ice core records collected from Aurora peak.

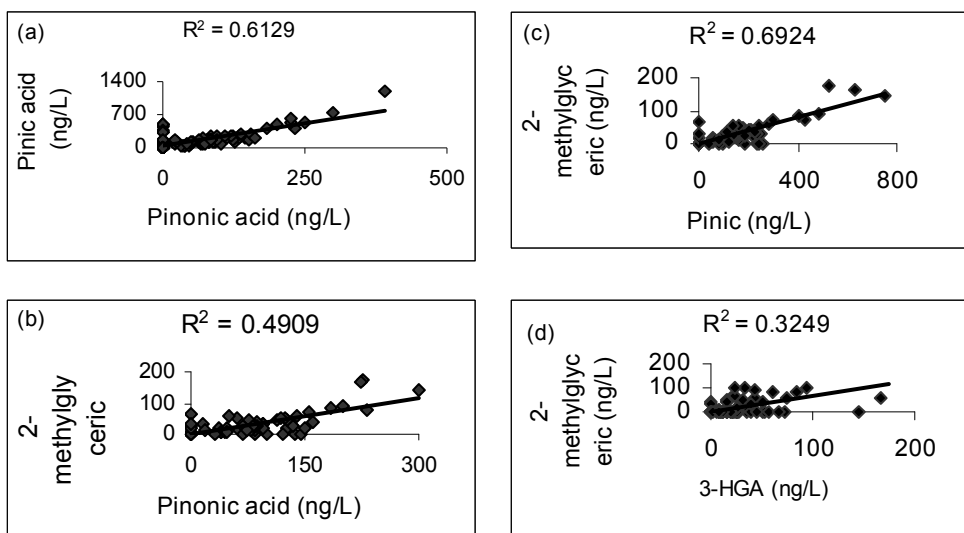


Figure 3. Correlation between the concentrations of (a) Pinonic and Pinic acid, (b) Pinonic acid and 2-methylglyceric, (c) Pinic acid and 2-methylglyceric, and (d) 2-methylglyceric and 3-hydroxyglutaric acid (3-HGA) in the Alaska ice core records collected from saddle of Aurora Peak.

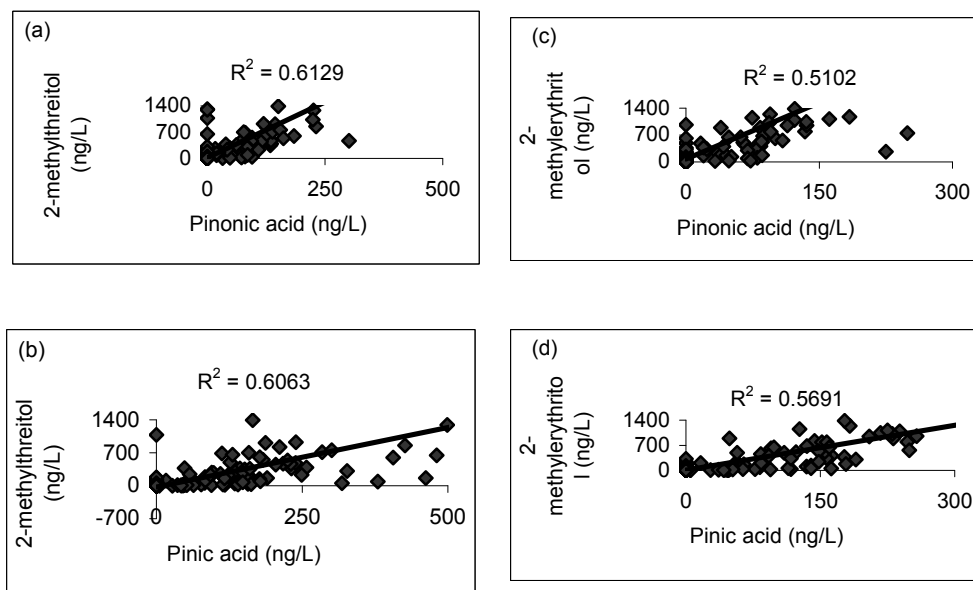


Figure 4. Correlation between the concentrations of (a) Pinonic acid and 2-methylthreitol, (b) Pinic acid and 2-methylthreitol, (c) Pinonic acid and 2-methylerythritol, and (d) Pinic acid and 2-methylerythritol in the Alaska ice core records collected from saddle of Aurora Peak.

Chapter 7. Climate signal recorded in the dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls from the Kamchatka-Peninsula (300 yrs) for an ice core: Climate change implications in the Northern Hemisphere

7.1. Introduction

Low molecular weight dicarboxylic acids, ω -oxocarboxylic acids and α -dicarbonyls for an ice core are produced in the atmosphere by photochemical oxidation of organic compounds and direct and indirect emission from anthropogenic and biogenic sources in the continent and marine atmosphere and deposited and/or incorporated in the ice sheet/snow-glaciers [Grosjean *et al.*, 1978; Kawamura *et al.*, 1996a, 1999, 2001]. For instance, acetylene (C_2H_2) can lead to oxalic acid (C_2) via α -dicarbonyls (e.g., glyoxal; Gly) as intermediate compound [Warneck, 2003]. Acetylene is associated with human activities and vertically plausibly well mixed [Blake *et al.*, 1997; Warneck, 2003] and long lived (more than two months) in the remote marine atmosphere [Kanakidou *et al.*, 1988]. On the other hand, ethene (C_2H_4) and phenolic compounds are produced from sea surface water [Warneck, 2003; Carlson, 1982a, 1982b, 1988] by bubble bursting mechanism [Marty *et al.*, 1979], and can be considered as biogenic signature in remote marine atmosphere, which can be further oxidized to ω -oxocarboxylic acid (e.g., glyoxylic acid; ωC_2) and phthalic acid (Ph) respectively. Oxalic acid (C_2) is the final oxidation product of acetylene and ethene. Hence, low molecular weight dicarboxylic acids (DCAs; e.g., C_2), ω -oxocarboxylic acids (e.g., ωC_2) and α -dicarbonyls (e.g., Gly)

are associated with natural and anthropogenic climate change [Kawamura and Gagosian, 1987, 1990; Kawamura et al., 1996a, 2001; Pokhrel et al., 2014a, 2014b].

There are some studies of paleo-geochemical cycles of inorganic compounds [Mayewski et al., 1986; Legrand, 1995; Mayewski and Legrand, 1990; Kaspari et al., 2009a, 2009b; Holdsworth et al., 1996; Grigholm et al., 2009; Goto-Azuma and Koerner, 2001] and organic compounds, [Holdsworth et al. 1996; Legrand and De Angelis, 1995, 1996; Jaffrezo et al., 1998; Kang et al., 2001; Kawamura et al., 1999, 2001, 2012a], which are associated with biogenic, and anthropogenic sources by using ice core. Two studies for ice core of the Greenland Site-J [Kawamura et al., 2001] and recently, the Aurora Peak of Alaska (APA) [Pokhrel et al., 2014a] have been reported for water-soluble dicarboxylic acids, ketoacids and α -dicarbonyls. These two studies showed that they are associated with multi-decadal climate change variability. Thus, this study will more sharpen the interactions and link between organic compounds and climate change variability. We collected ice to better understand the sources, atmospheric transformation processes of diacids and related compounds for an ice core from northwest of Pacific region.

7.2. Samples and Analytical Procedures

An ice core (301 years, ~151 m long) was drilled in June 1998 at an ice cap on the Gorshkov crater at Ushkovsky of the central part of this Kamchatka-Peninsula, the Russian Federation (UKPRF) (altitude: 3903 m, 56° 04'N and 160° 28'E). The ice core chronology were determined by oxygen isotope ratio ($\delta^{18}\text{O}$) from surface to 103.5 meter in depth, and two-dimensional thermodynamic coupled model for 103.5 to 151 m. Ice

core was estimated to be ca. 301 year old, i.e., 1697 AD [*Salamatin et al.*, 2000; *Shiraiwa et al.*, 2001]. Age determination error was estimated to be ± 2 years for surface level to 103.5 m and more than ± 2 years for 103.5 to 151 m [*Shiraiwa and Yamaguchi*, 2002; *Sato et al.*, 2014]. The ice core sample was cut into ~ 50.0 cm long pieces and brought to the laboratory of Institute of Low temperature Science (ILTS), Hokkaido University, Japan and stored in a dark and cold room having temperature -20°C until analyses. 109 ice sections were analyzed, which is equal to $\sim 39.0\%$ of 151 m long ice core.

10 mm (± 2 mm) surfaces of ice core samples were shaved off on a clean bench at -15°C cold room using a ceramic knife to avoid the possibly adsorbed contaminations during sample collection and transport to the ILTS, using the method previously reported [*Legrand et al.*, 1993; *Savarino and Legrand*, 1998; *Kawamura et al.*, 2001, *Pokhrel et al.*, 2014a]. Briefly, these scraped samples were kept in a pre-cleaned Pyrex beaker with Teflon tape, inside standardized clean-cold room having temperature -15°C for 24 hour. After 24 hour, samples were transferred into brown glass bottles and mercury chloride was added [*Kawamura et al.*, 2001].

We used the methods to analyze organic compounds as previously reported elsewhere [*Kawamura and Gagosian*, 1987; *Kawamura and Ikushima*, 1993; *Kawamura et al.*, 1996a, 2001; *Pokhrel et al.*, 2014a]. Briefly, 100 ml of melt water (pH was adjusted in between 8.50-9.0 using 0.1 M KOH) were concentrated until dryness and derivatized with ~ 0.25 ml of 14.0% boron trifluoride (BF_3)/n-butanol at 100°C for 1 hour [*Kawamura et al.*, 2001]. After extraction of derived butyl esters and dibutoxy acetals with n-hexane, derivatives of low molecular weight dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls were determined using a Hewlett Packard (HP 6890) capillary gas

chromatograph (GC). The GC peaks were identified by comparison with GC retention times of authentic standards chromatograph and confirmed by mass spectral analyses using a GC/MS system.

Before analysis of real ice core records, “recovery test” was completed. The recoveries were above 88% for oxalic (C_2) and more than 90% for malonic (C_3), succinic (C_4), glutaric (C_5) and adipic (C_6) diacids [Pokhrel *et al.*, 2015a]. We also conducted reproducibility test. The analytical errors in the triplicate analyses were 3.0, 3.3, 2.7, 3.4 and 4.0% for C_2 , C_3 , C_4 , C_5 , and C_6 for this study, respectively. The procedural/laboratory blank levels in comparison to real samples were 1.4, 0.05, 0.04, 1.3, 1.4, and 0.0% for C_2 , C_3 , C_4 , C_5 , C_6 and phthalic acid (Ph), respectively. Concentrations of all species were corrected for procedural lab blanks.

7.3. Results

7.3.1. Molecular Composition and Concentration of Organic Compounds

We detected more than 33 compounds from this ice core records (Table 1). The average molecular distribution is predominated by C_2 , which is followed by C_4 and C_3 . First time, we detected such type of molecular distribution for historical ice core records. Similarly, relative abundance of C_2 is followed by C_4 and C_3 to total dicarboxylic acids (not shown in Table). Ketocarboxylic acids also showed somewhat different molecular distribution ($\omega C_2 > \omega C_8 > \omega C_9$) from other ice core records of Greenland Site-J ($\omega C_2 = \omega C_4 > \omega C_3 > \omega C_9$) and APA ($\omega C_9 > \omega C_2 > \omega C_4$) [Kawamura *et al.*, 2001; Pokhrel *et al.*, 2015a]. We detected concentration of unsaturated aliphatic diacids (maleic, fumaric, and methylmaleic) and/or aromatic diacids (phthalic, isophthalic and terephthalic acid),

multifunctional dicarboxylic acids (malic, ketomalonic, and 4-ketopimelic), and also significant concentration of methylmalonic (iC₄), methylsuccinic (iC₅) and 2-methylglutaric (iC₆).

In this study, the average concentration (49.0 ng/g-ice) of total diacids and its related compounds (Table 1) is higher than Greenland Site-J [Kawamura *et al.*, 2001] ice core (11.1 ng/g-ice) and APA [Pokhrel *et al.*, 2014a] ice core (32.2 ng/g-ice). Similarly, average concentration of ω -oxocarboxylic acids (4.28 ng/g-ice) is comparable to APA ice core (5.31 ng/g-ice), and 7th times higher than Greenland site-J (0.69 ng/g-ice). In addition, average concentration of α -dicarbonyls of APA (0.67 ng/g-ice) and Greenland site-J (0.47) are close to each other than this study (1.18 ng/g-ice). While, pyruvic (Pyr) acid (1.09 ng/g-ice) is close to APA ice core (1.43 ng/g-ice) and near about 5th times higher than Site-J ice core (0.23 ng/g-ice).

7.3.2. Historical Concentration Changes of Organic Compounds

The historical variation of short chain low molecular weight dicarboxylic acids (s-DCAs), i.e., C₂-C₅, and long chain low molecular weight dicarboxylic acids (l-DCAs), i.e., C₆-C₁₂ are fluctuated in similar ways to each other. Historical concentration trends of all these species (C₂-C₁₂) showed slightly higher spikes around 1725-1780, 1850-1900s, and gradually increasing after 1900–1990s (except for, C₁₀ and C₁₁) (Figure 3a-3kc). Interestingly, other species of diacids (4a-4j), ketocarboxylic acids (5a-5e), and α -dicarbonyls (5f-5g) showed similar historical concentration trends to each other. For instance, methylsuccinic (iC₅), 2-methylglutaric (iC₆), malic (M), methyl maleic (mM), 4-ketopimelic acid (kC₇), glyoxylic acid (ω C₂), 3-oxopropanoic acid (ω C₃; except for

1980s-1990s), ωC_4 (except for 1980s-1990s), and methyl glyoxal (MeGly) showed similar historical trends. Concentration ratios are increased around 1850s-1890s and after 1950s for ωC_2 /Gly, C_2 /Gly and C_2 /Pyr (Figure 6a-6d), suggest photochemical oxidation of precursors compounds and their reactions pathways [Kunwar and Kawamura, 2014]. Similarly, historical trends of all these organic compounds have covered the reconstructed Dalton, Damon and/or Gleissberg minima of solar total irradiance (STI). Furthermore, they are well correlated with Greenland temperature anomalies (GTA), Arctic Oscillation (AO/NAO), Pacific Decadal Oscillation (PDO), (Figure 7e-7h).

7.4. Discussion

7.4.1. Correlation Analyses: Possible Sources and Formation Mechanism

Atmospheric photochemical oxidation of longer chain diacids, ketoacids and α -dicarbonyls can lead to end product of oxalic acid (C_2). So it is reasonable to perform the correlation analyses (Table 2). C_2 is strongly correlated with precursor compounds (e.g., C_3 , C_4 , kC_3 , kC_7 , F, mM, ωC_2 , ωC_3 , ωC_4 and MeGly) and branched saturated diacids (iC_4 - iC_6). This strong correlation indicates that chain reactions are involved for end product of C_2 . Moreover, there are strong correlations among C_6 , C_7 , C_8 , C_9 , Ph, ωC_9 , Pyr, Gly and MeGly, suggesting that they are to be formed from similar sources or same reaction pathways. For instance, 9-Oxononanoic (ωC_9) is formed during the oxidation of oleic acid ($C_{18:1}$) and oxidized into azelaic acid (C_9). This, $C_{18:1}$ is emitted from the marine phytoplankton through bubble bursting mechanism and terrestrial higher plants (all references are cited in later sections, e.g., section 4.3).

7.4.2. Principal Component Analyses

We used principal component analyses (PCA) to find out the multiple sources of these diacids and related compounds for an ice core ($n = 109$). Interestingly, there is high loading of C_6 , C_8 , C_9 , C_{10} , Ph, iPh and ωC_9 in component 1 (Table 3). Special tracers of marine emission are C_8 , C_9 and ωC_9 from unsaturated fatty acids ($C_{18:1}$) indicates marine sources and similar reaction pathways for these compounds. Component 2 shows high loading of C_2 - C_5 , ωC_2 and MeGly. This doesn't detect any special anthropogenic or biogenic emission rather than similar reaction pathways of photochemical oxidation [Kawamura and Sakaguchi, 1999; Pavuluri et al., 2010]. C_6 Ph, Pyr and Gly were considered from dual sources of anthropogenic and biogenic activities as we have discussed later sections [Kawamura et al., 1996a; Carlson 1982a, 1982b, 1988]. Component 3 and 4 are demonstrating that they are formed by photochemical oxidation of precursor compounds before and after industrial revolution (at least in 1900s) could be from dual sources. For instance, Kawamura et al. [2012a] found significant concentration of levoglucosan, dehydroabietic, vanillic, p-hydroxybenzoic acid and other carbonaceous compounds in the same ice core.

7.4.3. Origin of Dicarboxylic Acids, Ketocarboxylic Acids and α -Dicarbonyls

Low molecular weight dicarboxylic acids, ketocarboxylic acids (ωC_2 - ωC_9 and Pyr), α -dicarbonyls (Gly and MeGly) and related compounds can be originated from primary and secondary sources of fossil fuel combustion [Kawamura and Kaplan, 1986; Kerminen et al., 2000; Legrand, et al., 2007], biomass burning activities [Jaffrezo et al., 1998; Andreae, 1988; Lefer, 1994; Kawamura et al., 2013] and terrestrial higher plants and

marine phytoplankton [*Kawamura et al., 1996a; Kawamura and Gagosian, 1990; Kawamura et al., 2001*]. For instance, phytoplankton can emit unsaturated fatty acids and monocarboxylic acids from marine atmosphere [*Osada and Langway, 1993; Kawamura et al., 1999; Mochida et al., 2003a*]. Moreover, diacids and related compounds are derived by atmospheric photo-oxidation of volatile organic compounds (VOCs) and/or biogenic volatile organic compounds (BVOCs) such as isoprene, alcohols, ketoacids, monoterpenes and sesquiterpenes [*Mochida et al., 2003b; Talbot et al., 1995; Lim et al., 2005; Carlton et al., 2007*]. Terrestrial higher plants and/or vegetations and marine biota are the emitters of VOCs and BVOCs [*Andreae et al., 1987; Talbot et al., 1995; Lim et al., 2005; Carlton et al., 2007; Limbeck et al., 2001; Kawamura et al., 2001*].

7.4.3.1. Shorter-Chain Diacids (C₂-C₄)

As stated above, molecular distribution (C₂ > C₄ > C₃) and relative abundance (C₂ > C₄ > C₃) (not shown in Table) are slightly different from that of ice core from the Greenland Site-J [*Kawamura et al., 1999*] and the Aurora Peak of Alaska [*Pokhrel et al., 2014a*]. For instance, the Aurora Peak of Alaska (APA) has predominance of C₂ (ave. 7.2 ± 4.2 ng/g-ice), which is followed by C₆ (ave. 4.9 ± 10.5 ng/g-ice) and C₄ (ave. 4.3 ± 3.2 ng/g-ice). On the other hand, APA showed high relative abundance of C₂, which is followed by C₄ and C₆. In contrast, Greenland site-J ice core showed predominance of C₄ (ave. 4.8 ng/g-ice), which is followed by C₂ (ave. 2.1 ng/g-ice) and C₃ (ave. 0.77 ng/g-ice). It should be noted that, many ice core sections of this study have C₄ dominations from surface to 151 m in depth. Molecular distribution, relative abundance and average

concentration of C₂ from this study suggest the importance of atmospheric transport followed by deposition, and incorporation of these organic species to the snow particles via atmospheric oxidation. Thus, emission, atmospheric transport, deposition and/or incorporation and the atmospheric oxidizing capability in the western Pacific regions are higher than other ice core studies in the NH (it will be more discussed in section 7).

There are similar historical trends of s-DCAs to each other (Figure 3a-3d), demonstrating that there could be similar reaction pathways and/or same source likely to be pyruvic acid (Pyr), glyoxal acid (Gly), methylglyoxal (MeGly), glyoxylic acid (ω C₂), 3-oxopropanoic acid (ω C₃), 4-oxobutanoic acid (ω C₄), mid-chain keto and hydroxy acids, oxomalonic acid (kC₃) and malic acid (hC₄) together at a time [Kawamura *et al.*, 1996a, 1996b; Nishikiori *et al.*, 1997; Sempere and Kawamura, 1994; Kunwar and Kawamura, 2014]. These precursor compounds are contributed to the s-DCAs as a biogenic and/or anthropogenic precursor compounds for an ice core (e.g., Greenland Site-J) [Legrand *et al.*, 2007; Kawamura *et al.*, 2001, 1999].

Here, it should be noted that succinic acids (C₄) can be produced by photochemical oxidation of l-DCAs including keto group at C-4 position [Kawamura *et al.*, 1996a; Sempere and Kawamura, 2003] and/or mid chain keto and hydroxyacids [Kawamura and Gagosian 1987, 1990] and oak wood burning during forest fires [Rogge *et al.*, 1998]. Again C₄ would be further oxidized to oxalic acids (C₂) under photochemical oxidation [Kawamura *et al.*, 2001]. In addition, malonic acid (C₃) can be emitted by pinewood burning [Rogge *et al.*, 1998; Legrand *et al.*, 2007; Kawamura *et al.*, 2013]. C₄ and C₃ are further oxidized to C₃ and C₂, respectively, with their intermediate compounds of malic (hC₄) and oxomalonic acid (kC₃). The historical concentration trends of kC₃, hC₄ and kC₇

are similar to C₂ and C₃ and C₄, respectively (Figure 4h-4j). The similar historical trends of C₂ and its precursor compounds such as hC₄, kC₃, and kC₇ can imply secondary production of C₂ through photochemical degradation of precursor compounds [Legrand *et al.*, 2007].

Similar chain reactions of s-DCAs could be occurred in cloud water droplets in aqueous phase reaction [Warneck *et al.*, 2003; Legrand *et al.*, 2007; Carlton *et al.*, 2007]. Thus, we can easily assume that in-cloud oxidation may occur in the snow particles in aqueous phase reaction during cloud condensation process. For instance, Legrand *et al.* [2007] clearly mentioned that s-DCAs could be associated with cloud water droplet. The Pacific Ocean and the Sea of Okhotsk has surrounded this sampling site. Thus, Kamchatka-Peninsula (KP) is strongly influenced by marine atmospheric circulation from the Pacific Ocean and the Sea of Okhotsk (>60%) rather than terrestrial atmospheric circulation from eastern Siberia [Numaguti, 1999]. For instance, more than 80% winter precipitation and 50% of summer precipitation reached over UKPRF from the North Pacific regions only [Numaguti, 1999; Sato *et al.*, 2014]. Moreover, backward trajectory analyses showed that main sources of atmospheric aerosol loading over UKPRF are North Pacific, the Arctic Ocean and eastern Siberian regions [Kawamura *et al.*, 2012a].

Comparison of this study with APA and Greenland Site-J showed that C₂ and C₄ are playing hide and seek under similar marine biogenic sources, terrestrial higher plants and vegetation emission via photochemical oxidation of precursor compounds and similar reaction pathways in the snow particles and/or KP's glaciers. It should be noted that, we detected significant concentration of s-DCAs (C₂-C₅) before industrial revolution and they have similar historical trends each other since 1700-1900 AD, which is the

indication of biogenic signature as well as same reaction pathways via photochemical oxidation of their precursor compounds. Thus, predominance of C₂ followed by C₄ and C₃ can lead to consider that major portions of C₂, C₃ and C₄ could be originated by naturally derived organic precursor species including biomass burning in Siberian regions rather than fossil fuel combustion in the NH [*Kang et al., 2001; Legrand et al., 2007; Kawamura et al., 2012a; 2012b; Kawamura and Gagosian, 1987*].

7.4.3.2. Longer-Chain Diacids (C₅-C₁₂) and Related Compounds

Zooplankton, phytoplankton and brown macro algae, cuticular materials-higher terrestrial plants signatures [*Stephanou and Stratigakis, 1993; Kawamura and Kaplan, 1986*], bacterial oxidation of plant-derived fatty acids in soils and biomass burning and fossil fuel combustion [*Kawamura and Gagosian, 1990; Kawamura et al., 1995a, 1995b*] can produce l-DCAs (C₅-C₁₂) and aromatic diacids i.e., phthalic (Ph), isophthalic (iPh) and terephthalic acid (tPh). First time, we detected predominance of suberic acid (C₈) (1.72 ng/g-ice), which is followed by adipic acid (C₆) (1.64 ng/g-ice) and azelaic acid (C₉) (1.15 ng/g-ice). The predominance of C₈ was not reported in previous ice core and aerosol studies in the NH (e.g., *Kawamura et al., 1996a, 1999, 2001; Kunwar and Kawamura, 2014*). In contrast, Greenland Site-J and APA have predominance of C₉ [*Kawamura et al., 2001; Pokhrel et al., 2014a*].

Particularly, C₆ and C₈ could be produced from C₉ by α -oxidation with OH radical [*Kawamura and Gagosian, 1987; Kawamura et al., 2001*]. Moreover, phthalic acid (Ph) comes from phenolic compounds, which are present in sea surface slicks [*Carlson, 1982a, 1982b, Carlson et al., 1988*] and injected to the atmosphere by bubble bursting

mechanism [Marty *et al.*, 1979]. Furthermore, we detected significant concentration of l-DCAs and aromatic diacids (e.g., Ph) before industrial revolution, which is the indication of biogenic signature of l-DCAs and aromatic diacids (e.g., Ph). Similar historical concentration trends of l-DCAs (C₆-C₁₂) and aromatic diacids (e.g., Ph) to each other (Figure 3e–3k and 4g) (except some points for undecanedioic, i.e., C₁₁ and dodecanedioic acid, i.e., C₁₂) suggest that aromatic diacids (e.g., Ph) has a biogenic sources. For instance, photooxidation of acetylene and ethylene and/or isoprene were contributed from marine atmosphere to these compounds [Warneck, 2000, 2003]. Significant average concentration of phthalic (Ph) of this study (2.57 ng/g-ice), is comparable to nine month observations of fresh snow at Dome Fuji Antarctica (ave. 2.16 µg/kg-ice) and APA (ave. 3.24 ng/g-ice), and more than 4 times higher than Greenland Site-J (ave. 0.56 ng/g-ice) ice core [Matsunaga *et al.*, 1999; Kawamura *et al.*, 2001; Pokhrel *et al.*, 2014a]. Greenland site-J and APA ice core have been discussed as a biogenic signature for these DCAs and aromatic diacids (e.g., C₆ and Ph).

Moreover, specific photochemical oxidation product of biogenic unsaturated fatty acids (C_{18:1}, C_{18:2} and C_{18:3}) is azelaic acid (C₉), containing a double bond at the C-9 position [Kawamura and Gagosian, 1987; Kawamura *et al.*, 1995b; 1999]. These unsaturated fatty acids are derived from sea water microorganisms by bubble bursting mechanism [Marty *et al.*, 1979], terrestrial higher plants emission and bacterial activities [Guenther *et al.*, 2006; Pavuluri *et al.*, 2010], meat cooking operation [Rogge *et al.*, 1991; Legrand *et al.*, 2007] and wood burning on forest fires and domestic wood fires [Rogge *et al.*, 1991, 1998; Legrand *et al.*, 2007]. Hence, predominance of C₈ suggests that atmospheric oxidation could be enhanced and/or l-DCAs might be affected on the

snow particles and/or glaciers surfaces may be after deposition under direct solar radiation (e.g., C_8 is higher than C_9). Again, significant concentration of C_9 suggests that direct and indirect long-range atmospheric transport of biological components of marine atmosphere was important for l-DCAs.

Thus, lower concentration (see Figure 3) for many decades of l-DCAs (C_6 - C_{12}) and phthalic acid (Ph) may be caused by a gloomy/low emission of fatty acids and phenolic compounds from seawater micro-layers. There could be realized by retreat of sea ice, associated with an enhanced photochemical oxidizing capability of the atmosphere in the NH for these compounds. For instance, Miller et al. [2007] confirmed the decline of sea ice cover by 3 to 4% in the Arctic Ocean from 1980 to 2000. Moreover western part of this sampling site is surrounded by the Sea of Okhotsk, which is covered by sea ice. It is more sensitive for marine biota than the open Seawater. Particularly, the underside of the sea ice can provide habitat for tiny algae, which is the base of a productive food web for marine environment (<http://www.oceansnorth.org/arctic-challenges>). In addition, Greenland Site-J and APA ice core showed somewhat higher concentration for these l-DCAs and unsaturated fatty acids [Kawamura et al., 1996b; 1996d; 1999; 2001; Pokhrel et al., 2014a] during such type of periods.

Sebacic acid (C_{10}), undecanedioic acid (C_{11}) and dodecanedioic acid (C_{12} ; which is detected first time from the ice core) are produced from terrestrial higher plant [Pavuluri et al., 2010; Kawamura et al., 1996a] and sea surface micro layers [Matsunaga et al., 1999]. Moreover, C_{11} is produced from photooxidation of $C_{18:1\omega7}$ monocarboxylic acid like vaccenic acid that is also available in the sea surface micro-layers [Matsunaga et al., 1999]. Thus, only few point did not match with higher spikes/periods of l-DCAs and Ph

suggests that molecular distribution of marine biogenic sources and higher terrestrial plants signature could be activated at a times and/or sources would have shifted, likely due to dynamical effect of wind circulation pattern from sea-air-land interaction (e.g., seasonal changes). In addition, northeast Asian atmospheric transport could be reached at a times. In contrast, historical concentration of l-DCAAs are similar to each other (e.g., C₆-C₉ and C₁₂), further suggest that UKPRF received more biogenic signatures rather than anthropogenic.

Concentration of iC₄ (0.33 ng/g-ice), iC₅ (0.99 ng/g-ice), and iC₆ (0.20 ng/g-ice) are higher than Greenland site-J (ave. 0.055, 0.28, 0.059 ng/g-ice) and comparable to Alaskan ice core (ave. 0.77, 0.34, 0.27 ng/g-ice). The historical concentration trends (iC₄, iC₅ and iC₆) (Figure 4a-4c) are somewhat similar to C₄-C₆ (Figure 3c-3e) and ω -oxocarboxylic acids (e.g., ω C₄ and ω C₅; not shown in figure). These results and correlations Table 2 suggest that branch chain diacid could be derived from terrestrial higher plants, biomass burning and marine atmosphere [*Kawamura et al., 2001; Pokhrel et al., 2014a*].

Maleic acid (M) can be formed from the oxidation of aromatic structures (e.g., Ph) in the marine atmosphere. Concentration of fumaric acid (F) is higher (ave. 0.58 ng/g-ice) than M (ave. 0.57 ng/g-ice), which is similar to APA concentrations order (0.32 and 0.15ng/g-ice for F and M, respectively). In contrast, Greenland site-J showed reverse order (0.08 and 0.10 ng/g-ice for F and M). This result suggest that photo-isomerization reaction of cis M to F could be more enhanced in lower latitudes than Greenland Site-J under the direct solar radiation. We detected higher concentration of methyl maleic, i.e. mM (0.24 ng/g-ice) than Greenland site-J (0.023 ng/g-ice) and lower than APA (0.30

ng/g-ice) ice core [Kawamura *et al.*, 2001; Pokhrel *et al.*, 2014a]. The historical concentration trend of mM is similar to methylglyoxal (MeGly) except for some points (Figure 4f and 5g), and correlations with other precursor compounds of diacids (Table 2) indicating that they may be derived from same source and could be from “in-cloud isoprene” oxidation product [Lim *et al.*, 2005] and/or similar reaction pathways of MeGly. In other words, subsequent SOA formation in the atmosphere during cloud formation process as intermediate product of isoprene, and is further oxidized to oxalic acid (C₂) in aqueous phase [Lim *et al.*, 2005; Warneck *et al.*, 2003; Ervens *et al.*, 2004].

7.4.3.3. ω -oxocarboxylic acids (ω C₂- ω C₉) and Pyruvic acid

Homologous series of ω -oxocarboxylic acids (ω C₂- ω C₉) is predominated by ω C₂, which is followed by ω C₈ and ω C₉ (Table 1). Meanwhile, Greenland Site-J showed predominance of ω C₂ (or ω C₄), which is followed by ω C₃, and then ω C₉ [Kawamura *et al.*, 2001]. On the other hand, APA ice core showed predominance of ω C₉, which is followed by ω C₄ and ω C₂ [Pokhrel *et al.*, 2014a]. Lim *et al.*, [2005] has reported “in-cloud” isoprene oxidation pathways producing glyoxylic acid (ω C₂) as a precursor compound of C₂. In addition, ω C₃, ω C₄ and ω C₉ could be formed in the marine atmosphere from the oxidation of unsaturated fatty acids [Kawamura *et al.*, 1996a; Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993; Kawamura *et al.*, 2001; Pavuluri *et al.*, 2010; Kunwar and Kawamura, 2014] during bubble bursting process [Marty *et al.*, 1979]. Moreover, ω -oxocarboxylic acids (i.e., ω C₇, ω C₈ and ω C₉) are special tracers of biogenic emission (including forest fires) from terrestrial higher plants and marine atmosphere [Kawamura and Gagosian, 1987, Kawamura and

Ikushima, 1993; Kawamura et al., 1996a, 2001].

Similarly, the historical concentration trends of 5-oxopentanoic (ωC_5), 7-oxoheptanoic (ωC_7) and 8-oxooctanoic (ωC_8) (not shown in figure) are similar to C_5 - C_8 and correlations (table 2) and principle components (Table 3) suggesting that these compounds have similar sources [*Kawamura et al., 1999; Kawamura et al., 2001*]. Furthermore, we can not exclude that DCAs, oxoacids and α -dicarbonyls from biomass and biofuel burning [*Kawamura et al., 1996a; Kundu et al., 2010a; 2010b; Graham et al., 2002; Kawamura et al., 2012b; Miyazaki et al., 2009*] could be incorporated in the ice sheet/ice particles specially after industrial revolution via long range atmospheric transport from East Siberian regions [*Kawamura et al., 2012a*]. It should be noted that the historical concentration trends of ωC_2 and MeGly are somewhat similar to each other, and correlation is also strong ($R^2 = 0.70$), which is to be in-cloud isoprene oxidation product [*Lim et al., 2005*]. Moreover lifted carbonyls from lower to higher troposphere can also produce C_2 and ωC_2 in aqueous phase oxidation, when the tropospheric temperature decreases and humidity increases [*Warneck, 2003; Carlton et al., 2007; Legrand et al., 2007; Kawamura et al., 2013*].

Pyruvic acid (Pyr) can be originated from oxidation of phenolic groups [*Grosjean, 1983*], isoprene and/or ‘in-cloud isoprene’ [*Andreae et al., 1987; Talbot et al., 1995; Lim et al., 2005; Carlton et al., 2007*], aromatic hydrocarbons [*Kawamura et al., 1996a*], as well as oxidation of Gly and MeGly in heterogeneous aqueous phase [*Warneck, 2003; Carlton 2007; Kawamura et al., 2013*]. It should be noted that historical concentration trend (Figure 5e) showed higher spikes before industrial revolution (1700s-1850s). It would lead to source of photochemical oxidation of biogenic organic matter-isoprene

rather than fossil fuel combustion. In other words, Lim et al., [2005] has proposed for in-cloud isoprene oxidation pathways, in which oxidation product of gas-phase isoprene dissolve in to atmospheric cloud water and react with OH radical producing oxalic acid (C_2), glyoxylic acid (ωC_2), pyruvic acid (Pyr) and others related compounds. The historical concentration trend of Pyr (Figure 5e) is somewhat similar to Gly, MeGly, C_3 , C_4 , total diacids and ωC_2 could be due to photochemical oxidation products of organic precursors such as isoprene [Andreae et al., 1987; Talbot et al., 1995; Carlton et al., 2006, 2007]. Hence, concentration of pyruvic acid (1.09 ng/g-ice) is close to APA (1.43ng/g-ice) and higher than Greenland Site-J (0.23 ng/g-ice) [Pokhrel et al., 2014a; Kawamura et al., 2001] to act as a precursor for final product of DCAs.

7.4.3.4. Glyoxal and Methylglyoxal

α -dicarbonyls (glyoxal and methylglyoxal) are semi volatile organic compounds. They can be produced by atmospheric oxidation of aromatic hydrocarbons from benzene, toluene, xylene, alkenes and p-xylene [Smith et al., 1998; Christensen et al., 2000; Volkamer et al., 2001, 2006]. Moreover, α -dicarbonyls can be emitted by biogenic combustion via atmospheric oxidation processes in heterogeneous aqueous phase [Kunwar and Kawamura, 2014; Kleindienst et al., 2004; Warneck, 2003; Christensen et al., 2000], and oxidation of isoprene in the presence of OH radicals [Carlier et al., 1986; Spaulding et al., 2003; Ervens et al., 2008; Carlton et al., 2009]. Particularly, α -dicarbonyls was more enhanced than its background level during agricultural biomass burning periods for aerosol sample. For instance, glyoxal (Gly) and methylglyoxal (MeGly) were further oxidized to C_2 , ωC_2 and Pyruvic acid (Pyr), when humidity was

increased over the Mt. Tai, east China [Kawamura *et al.*, 2013; Fu *et al.*, 2012], it could be under heterogeneous aqueous phase [Warneck, 2003].

Moreover, concentration ratios of ω C₂/Gly (range: 0-68, ave. 4), C₂/Gly (range: 0-642, ave. 41) and C₂/Pyr (range: 0-423, ave. 55) have been increased (Figure 6a-6c) during heavy biomass burning period of 1850s-1890s in the NH [Legrand and De Angelis, 1996; Holdsworth, *et al.*, 1996] suggesting that biomass burning may be important source of DCAs. Interestingly, these concentration ratios have good agreement with reconstructed Arctic temperature departures (e.g., C₂/Pyr) [Jacoby and D'Arrigo, 1989; Jacoby *et al.*, 1999]. Arctic Oscillation-related surface air temperature is correlated elsewhere [e.g., Jacoby *et al.*, 1999; D'Arrigo *et al.*, 2003]. On the other hand, Greenland Site-J (e.g., C₉) has also good agreement with this temperature [Jacoby and D'Arrigo, 1989; Kawamura *et al.*, 1999]. These results indicate the enhanced photochemical capability of the atmosphere and/or paleo-aqueous phase heterogeneous reactions, SOA from isoprene in the terrestrial, marine biota and also biogenic combustions could be major sources of α -dicarbonyls and related compounds [Myriokefalitakis *et al.*, 2008; Wittrock *et al.*, 2006; Simoneit *et al.*, 2004; Grosjean *et al.*, 2000].

7.4.4. Climatic Window and Response of Organic Compounds

Dicarboxylic, ketocarboxylic acids and α -dicarbonyls are potentially important to find out the climate change variability. They are imprinted as air-sea interaction, atmospheric transport, sources and paleo-oxidizing capability of the atmosphere.

7.4.4.1. Response of Ambient Atmospheric Temperature

The historical variation of total dicarboxylic acids, ω -oxoacids, and α -dicarbonyls showed lower concentration around 1800 and 1900 (except for 1903, 1907 and 1921) than its background level (Figure 7a-7c). These periods are confirmed by prolonged cold climate periods [Groverman and Landsberg, 1979, Jacoby and D'Arrigo, 1989; Mann and Jones, 2003; Mann et al., 2008, 2009; NASA (Glossary, I-M, Retrieved 28, February 2011)]. For instance, there is sharp decrease in temperature between 1800-1820 and known as the cold decade as “year without summer” in 1816 [Landsberg and Albert, 1974; Jacoby and D'Arrigo, 1989]. By using, ice melting proxy records, Paterson et al. [1977] reported cold period between late 17th to early 1800th [Williams and Wigley, 1983; Jacoby et al., 1985; Jacoby and D'Arrigo, 1989].

Moreover, relations between 9 points running mean (9-RM) of extra tropical northern Hemispheric temperature (ET), i.e., 9-RM ET [e.g., Wilson et al., 2007] with 9-RM of C₃ (R = 0.72), 9-RM of C₄ (0.81), intermediate compounds, e.g., 9-RM of kC₇ (0.81), 5-RM of ET with 30-RM of C₁₂ (0.71) and 11-RM of ω C₂ with 11-RM of ET (0.63) showed positive (Figure 3b, c, k, 4j, 5a). It should be noted that C₃ is hardly derived from the oxidation of aromatic hydrocarbon (Figure 3c). Similarly, correlation of intermediate compounds between C₂, C₃ and C₄, i.e. ketomalonic (kC₃) and malic (hC₄) are also well correlated with this temperature (ET). Wilson et al. [2007] reported that ET has positive correlations with more than 25 different tree ring proxy records of the world, e.g., European Alps (0.67), western Siberia (0.61), Mongolia (0.70), Nepal (0.49), Northern Yukon (0.60), Wrangell Mountains (0.60), British Columbia (0.77), Idaho (0.41) and Northern Quebec (0.42) (Wilson et al., 2007, references therein). These results suggest

that sea-air interaction; atmospheric transport, production rate and/or atmospheric oxidizing capability and sources of organic compounds (e.g., Figure 7a-7c) are associated with time series of climate change variability in the NH.

7.4.4.2. Response of Solar Irradiance

Solar total irradiance (STI), Northern Hemispheric temperature anomalies and summer temperature anomalies are correlated elsewhere [*IPCC, 1992; Bradley and Jones, 1993; Lean et al., 1995, 2005*]. The good correlations (R^2 ; 0.86 and 0.75) were observed between NH surface temperature and STI since 1610s-1800 and 1800-2000 [*IPCC, 1992; Bradley and Jones, 1993; Lean et al., 1995, 2005*]. Particularly, Maunder Minima has strong relation with the NH equilibrium surface temperature changes [*Eddy, 1976; Lean et al., 1995; Rind and Overpeck, 1993*]. This indicates that surface and lower tropospheric temperature response the solar forcing (e.g., STI). Thus, solar irradiance couple with sea-air-land interactions and cloud covers distributions [*Lean et al., 2005; Lean, 2010; Rind and Overpeck, 1993; Meehl et al., 2003, 2013*]. Moreover, solar irradiance can effect ozone concentration in the stratosphere [*Haigh, 1999*] and finally creating stronger tropospheric wind [*Shindell et al., 2001; Koder and Kuroda, 2002*], which can alter the periodic climate variability, e.g., NAO/AO, ENSO, and storm tracks strength i.e., precipitation variability) [*Lean et al., 2005; Lean, 2010; Meehl et al., 2003, 2009; Lockwood, 2012*]. In addition, 10-year running mean of STI has strong correlation (e.g., $R^2 = 0.79$) with the Arctic air temperature departure compared to greenhouse gases ($R^2 = 0.22$) [*Soon, 2005; Karner, 2002; Polyakov et al., 2003*].

Historical lower spikes (~1780s-1830s) of diacids and related compounds (e.g.,

Figure 7a-7c and 7f) reveals a long period of Dalton solar minima (~ 1780s-1830s) [Maunder, 1890, 1922; Lean *et al.*, 2005; Lean, 2010]. Meanwhile, lower spikes of diacids covered other solar activities such as Damon solar Minima (1890s-1920s), except for, few point (e.g., 1907 and 1921) and/or Gleissberg sunspots minima (1889-1902) [Gleissberg, 1939; Ahluwalia and Jackiewicz, 2011; Lean *et al.*, 2005, Lean, 2010; Trouet and Taylor, 2009]. Particularly, 52 and 31% of temperature change since 1910-1960 and 1970-1999, which was accounted by change in solar luminosity, respectively [Lockwood *et al.*, 1999]. Moreover, Scafetta and West (2007) estimated 50 and 25-35% warming since 1900 and 1980 by this STI, respectively. Moreover, relation between 5-RM of STI [e.g., Lean 2000] with 11-RM of C₃ (0.78), 15-RM of C₁₂ (0.70), end product of oxocarboxylic, i.e., 11-RM of ωC₂ (0.77) and other compounds are also well correlated. These results suggest that atmospheric oxidizing capability for these diacids are associated with radiative forcing.

It should be noted that winter Pacific/North American climate sensitivity index (PNA/PNAI) is positive during Dalton and Damon solar minima. Higher PNA index are strongly associated with the deepening of the Aleutian Low [Trouet and Taylor, 2009]. This PNA activity is associated with decadal modulation of ENSO (<http://www.pacificstormsclimatology.org/index.php?page=glossary>). Series of Aleutian Low can drive prevailing East Asian winds towards American west rather than Northwest Pacific regions. In other words, Aleutian Low would mix continental and marine air mass, and more drive prevailing westerly winds from the Northwestern Pacific to the Northwestern American continents (<http://www.seasonsintthesea.com/may/phys.shtml>), which can intensify the positive PNAI over American west [Trouet and Taylor, 2009; Harvey and Hitchman,

1996; Harvey *et al.*, 1999]. This result suggests that concentration of these diacids could be more diluted by this AL pressure system and/or prevailing westerly wind could be shifted (e.g., weaken of westerly wind) from Kamchatka-Peninsula's sky

[<http://www.arcus.org/synthesis2k/Micalake/index.php>].

These historical similarities of diacids and STI including Northern Hemispheric temperature anomalies are not only coincidence for this study. For instance, oxalic acid (C_2) carbon/total organic carbon (TOC) (i.e., C_2/TOC) ratio of Greenland Site-J [Kawamura *et al.*, 2001] has good agreement with the NH temperature anomalies [Bradley and Jones, 1993] and reconstructed STI [Lean *et al.*, 1995]. Other s-DCAs have also similar agreement with NH temperature anomalies (except for some points) and STI. Moreover, concentration of azelaic acid (C_9) for Greenland Site-J [Kawamura *et al.*, 2001] reflected the Maunder Minima. This C_9 has good correlation with recorded Arctic temperature departure [Jones and Kelly, 1983; IPCC, 1996] and reconstructed Arctic temperature departure [Jacoby and D'Arrigo, 1989]. These results suggest that atmospheric climate variability in perspective with the atmospheric oxidizing capability of the atmosphere could be associated with solar cycle periodicity and PNAI as well as glacier advances or glacier expansion and/or retreat of sea ice on decadal and centennial time scales in the NH [Kawamura *et al.*, 1996b, 1999; 2001; Pokhrel *et al.*, 2014a, 2014b].

7.4.4.3. Response of Greenland Temperature Anomaly

Further we have supporting information from Greenland study. There is relationship between Greenland temperature anomaly (GTA) and NAO [Kobashi *et al.*, 2013].

Meanwhile, NAO is a large-scale instability of atmospheric mass balance between the

mid-latitudes high and the Arctic low system. Moreover, positive NAO phase drive warm and wet winter in Europe and cold and dry winter in northern north Pacific region including North America to Greenland (<http://www.ldeo.columbia.edu/res/pi/NAO>). The historical trends of diacids compounds are somewhat similar to reconstructed GTA (Figure 7a, b, c and 7e), which primarily reflects Arctic Oscillations (AO). Organic compounds are to be transported and deposited and/or incorporated or vice-versa (i.e., drained out from the KP's atmosphere) to snow particles and could be associated with long-range atmospheric transport due to influence of AO/NAO.

Hence, relations between GTA with these compounds (Figure 3, 4, 5, and 7a, b, c and 7e) have anti correlations (except for C_{12} and ωC_2). For instance, 21-RM of GTA with 30-RM of C_2 (0.59), C_9 ($R=0.62$), C_2 - C_{12} (0.50), total annual dicarboxylic acids (0.71), M (0.62), F (0.62), Ph (0.43), ωC_2 (0.47), ωC_4 (0.69), ωC_8 (0.73), ωC_9 (0.56), total ω -oxocarboxylic acids (0.65), Pyr (0.58), Gly (0.28) and MeGly (0.50) have anti correlations. Similarly, 9-RM of GTA with intermediate compounds, e.g., 11-RM of hC_4 (0.27) and kC_7 (0.44) also showed anti correlations. This agreement further suggests that concentrations of diacids are increased with AO negative index (Figure 7a-7c and 7e). Trend of δD (Figure 6d) same ice core has followed multi-decadal climate oscillations, e.g., PDO and North Pacific Gyre Oscillation (NPGO) (*Sato et al., 2014; Di Lorenzo et al., 2008, references therein*) suggest that historical trend of δD indicate the extra tropical North Pacific surface climate conditions (*Sato et al., 2014; Smith et al., 2008*). For instance, correlation coefficient (R) of annual mean of δD and NPGO (*Di Lorenzo et al., 2008*) is 0.70 ($p < 0.10$). Moreover δD records are correlated with extended reconstructed sea surface temperature of the mid to high latitude North Pacific (30-45° N,

165- E- 165° W), which can represent the sea surface temperature anomaly and PDO (Sato *et al.*, 2014, *reference therein*).

Briefly, North Atlantic oscillation (NAO) and/or winter North Atlantic oscillation (wNAO), El Nino/Southern Oscillation (ENSO) and precipitation are associated with natural climate variability in the NH [Lean *et al.*, 2005; Lean, 2000; Lean, 2010; MacDonald and Case, 2005; Meehl *et al.*, 2013, 2009; Gershunov and Barnett, 1998; Trouet *et al.*, 2009; Trouet and Taylor, 2009]. In addition, wNAO assembled more atmospheric aerosols loading over western Pacific region (Kamchatka-Peninsula) rather than NAO (i.e., southwestern air mass and Polar air mass intrusion along the wNAO's path in the NH) [Trouet *et al.*, 2009]. Such type of climate variability from oceanic and atmospheric cycle can alter the concentration of organic compounds in the NH [Kawamura *et al.*, 1999; 2001; Pokhrel *et al.*, 2014a, 2014b]. For instance, 21-RM of PDO [Mac Donald and Case, 2005] with 15-RM of C₄ (0.71), 30-RM of C₂-C₁₂ (0.71), 30-RM of M (0.71), 30-RM of kC₇ (0.74) and 30-RM of MeGly (0.77) are well correlated. Moreover, other compounds, e.g., Ph, Gly and intermediate compounds, e.g., hC₄ and kC₃ showed positive correlations. Similarly, 15-RM of NAO [e.g., Trouet *et al.*, 2009] with intermediate compounds, e.g., 30-RM of hC₄ (0.67), 30-RM of kC₃ (0.47) have positive correlations (Figure 7h). It should be noted that 15-RM of NAO with 30-RM of C₄ (0.61), 30-RM of M (0.64) and MeGly (0.70) and other compounds also showed anti-correlations reveals the atmospheric transport during NAO positive phase further suggest that oxidizing capacity of the atmosphere (i.e., photochemical ageing) could be altered with the climate periodicity. Hence, correlations of these compounds with PDO, NAO, GTA, Northern Hemispheric temperature (ET), and STI strongly

suggest that organic compounds were likely to be linked with North Pacific index (NPI) and/or PDO, NAO and/or GTA.

These relations further suggest that diacids and related compounds are to be coupled with periodicity cycle of PDO, NPGO and AO at times. These compounds are imprinted for an ice core of Kamchatka as sea to air emission followed by subsequent long-range atmospheric transport and/or atmospheric oxidation, deposition and/or incorporation. Hence, dicarboxylic acids, oxocarboxylic acids and α -dicarbonyls of Kamchatka, Greenland Site-J and organic compounds of the Aurora Peak of Alaska (e.g., Pokhrel et al., 2014a and 2014b) reveal the sensitivities of response to the large-scale climatic periodicity in the North Pacific regions at times. There is another possibility that source should be different and/or some climate change forces/external force disrobed these compounds from this sampling site before precipitation. Special regional/local atmospheric activities over the northwestern Pacific region may restrict and/or may enhance these compounds for lower to higher spikes since 1700s-1900s. Hence, we hope that some discrepancy between the historical trends of dicarboxylic acids, ω -oxocarboxylic acids and α -dicarbonyls, and climatic periodicity sensitivities will be more disclosed by some other ice core studies from the Southern Hemisphere in perspective with the effect of climatic periodicity.

7.5. Conclusions

Organic compounds are derived from atmospheric photochemical oxidation of biogenic precursor compounds rather than human activities and/or enhanced sea-air flux of unsaturated fatty acids could be more activated as precursor compounds. Average concentration of these compounds showed that their source strength, atmospheric transport, wet and dry deposition and/or incorporation, and photochemical oxidation capability of the lower atmosphere is higher than the Greenland Site-J and the Aurora Peak of Alaska. Historical concentration trends of these compounds are fluctuated in similar ways with maxima at 1725-1775, 1825-1875, and 1950s-1990s and minima around 1775-1825 and 1875-19950 and they are coupled with periodicity cycle of PDO (ENSO), AO (wNAO), PNA and/or NPGO, and Northern Hemispheric (NH) temperature departure suggest that concentration are to be associated with land-sea-air interaction under these periodicity.

Lower concentration of these organic compounds suggests that the climate system interactions between aerosols, clouds, and precipitation in the pristine atmospheric conditions may substantially differ from anthropogenic activities in the NH. They could be associated with atmospheric conditions rather than anthropogenic activities. For instance, Alaskan ice core, Greenland Site-J and this study did not represent significant effect (direct effect) of the intense biomass burning periods in the NH since 1850s-1910s. Moreover, lower concentration trends reflected the reconstructed Dalton, and Damon and/or Gleissberg sunspots minima. In addition, Alaskan ice core has good agreement with tropospheric lower temperature anomalies, which is calculated from NOAA'S TIROS-N weather satellite since 1979-2008, extra tropical temperature anomalies and

other climate periodicity cycles, and Greenland Site-J ice core (e.g., s-DCAs) showed Maunder minima, respectively. These results further suggest that polar organic compounds could be strongly associated with photochemical oxidation of biogenic precursor compounds with past oxidizing capacity of the troposphere. Above discussion can lead us to be noted that historical or proxy records obtained from ice core are another basic sources of polar organic compounds for shaping authority in past oxidizing capacity of the pristine lower troposphere in the NH.

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Table 1. Concentrations of dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid and α -dicarbonyls in ice core samples from Gorshkov crater at Ushkovsky of the Kamchatka-Peninsula, Russia, Federataion (UKPRF) in 1697-1997.

Concentrations (ng/g-ice)					
Compounds	Chemical formula	Aver	Mini	Maxi	SD
Oxalic (C ₂)	HOOC-COOH	13.4	BDL	59.6	11.4
Malonic (C ₃)	HOOC-CH ₂ -COOH	4.61	0.02	29.4	4.98
Succinic (C ₄)	HOOC-(CH ₂) ₂ -COOH	13.4	0.37	79.9	13.0
Glutaric (C ₅)	HOOC-(CH ₂) ₃ -COOH	1.96	0.06	11.9	2.01
Adipic (C ₆)	HOOC-(CH ₂) ₄ -COOH	1.64	0.06	21.0	3.05
Pimelic (C ₇)	HOOC-(CH ₂) ₅ -COOH	0.51	0.01	4.76	0.74
Suberic (C ₈)	HOOC-(CH ₂) ₆ -COOH	1.72	BDL	46.1	5.36
Azelaic (C ₉)	HOOC-(CH ₂) ₇ -COOH	1.15	0.07	16.8	1.98
Sebacic (C ₁₀)	HOOC-(CH ₂) ₈ -COOH	0.87	BDL	24.5	2.89
Undecanedioic (C ₁₁)	HOOC-(CH ₂) ₉ -COOH	0.47	BDL	21.1	2.24
DodecanedioicC ₁₂	HOOC-(CH ₂) ₁₀ -COOH	0.06	BDL	0.76	0.10
Methylmalonic (iC ₄)	HOOC-CH(CH ₃)-COOH	0.33	BDL	2.36	0.40
Methylsuccinic (iC ₅)	HOOC-CH(CH ₃)-CH ₂ -COOH	0.99	0.03	5.95	1.05
2-Methylglutaric (iC ₆)	HOOC-CH(CH ₃)-(CH ₂) ₂ -COOH	0.20	BDL	0.80	0.18
Maleic (M)	HOOC-CH = CH-COOH	0.57	0.01	4.04	0.65
Fumaric (F)	HOOC-CH = CH-COOH	0.58	BDL	10.3	1.10
Methylmaleic (mM)	HOOC-C(CH ₃) = CH-COOH	0.24	0.01	1.84	0.26
Phthalic (Ph)	HOOC-(C ₆ H ₄)-COOH	2.57	BDL	57.5	7.02
iPh		0.80	BDL	15.5	2.26
tPh		1.02	BDL	23.8	2.77
Malic (hC ₄)	HOOC-CH(OH)-CH ₂ -COOH	0.45	BDL	10.1	1.22
Oxomalonic (kC ₃)	HOOC-C(O)-COOH	0.24	BDL	9.61	0.94
4-Oxopimelic (kC ₇)	HOOC-(CH ₂) ₂ -C(O)-(CH ₂) ₂ -COOH	0.41	BDL	2.69	0.42
Total annual dicarboxylic acids		49.0	2.95	324	46.6
Glyoxylic (ω C ₂)	OHC-COOH	1.60	BDL	8.61	1.53
3-Oxopropanoic (ω C ₃)	OHC-CH ₂ -COOH	0.20	BDL	1.49	0.27
4-Oxobutanoic (ω C ₄)	OHC-(CH ₂) ₂ -COOH	0.57	BDL	5.77	0.97
5-Oxopentanoic (ω C ₅)	OHC-(CH ₂) ₃ -COOH	0.40	0.01	4.07	0.75
7-Oxoheptanoic (ω C ₇)	OHC-(CH ₂) ₅ -COOH	0.54	BDL	4.79	0.81
8-Oxooctanoic (ω C ₈)	OHC-(CH ₂) ₆ -COOH	0.94	BDL	10.4	1.75
9-Oxononanoic (ω C ₉)	OHC-(CH ₂) ₇ -COOH	0.92	BDL	32.3	3.26
Total annual ω-oxocarboxylic acids		4.28	0.03	59.0	6.53
Pyruvic (Pyr)	CH ₃ -C(O)-COOH	1.09	BDL	9.91	1.63
Glyoxal (Gly)	OHC-CHO	0.81	0.02	11.9	1.46
Methylglyoxal (MeGly)	CH ₃ -C(O)-CHO	0.38	BDL	1.66	0.32
Total annual α-dicarbonyls		1.18	0.12	12.1	1.54

Table 2: Correlation coefficients (R^2) for dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid and α -dicarbonyls (ng/g-ice) in the ice core from Gorshkov crater at UKPRF in 1697-1997.

	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	iC ₄	iC ₅	iC ₆	M	F	mM	Ph	iPh	tPh	hC ₄	kC ₃	kC ₇	ω C ₂	ω C ₃	ω C ₄	ω C ₉	Pyr
C ₂	1																								
C ₃	0.52	1																							
C ₄	0.55	0.84	1																						
C ₅	0.49	0.63	0.81	1																					
C ₆	0.20	0.14	0.25	0.66	1																				
C ₇	0.25	0.29	0.41	0.75	0.71	1																			
C ₈	0.12	0.00	0.05	0.45	0.91	0.56	1																		
C ₉	0.18	0.07	0.18	0.57	0.91	0.70	0.89	1																	
iC ₄	0.47	0.53	0.47	0.52	0.52	0.44	0.55	0.53	1																
iC ₅	0.33	0.78	0.84	0.74	0.21	0.40	0.03	0.15	0.43	1															
iC ₆	0.35	0.62	0.69	0.76	0.58	0.53	0.43	0.48	0.60	0.72	1														
M	0.12	0.22	0.26	0.16	0.02	0.07	-0.01	0.05	0.15	0.34	0.30	1													
F	0.23	0.07	0.20	0.51	0.77	0.55	0.82	0.85	0.50	0.12	0.38	0.05	1												
mM	0.60	0.58	0.73	0.79	0.59	0.62	0.41	0.54	0.47	0.57	0.68	0.20	0.47	1											
Ph	0.22	0.04	0.09	0.43	0.84	0.53	0.93	0.83	0.70	0.06	0.46	0.01	0.78	0.40	1										
iPh	0.17	-0.03	0.00	0.39	0.85	0.56	0.87	0.74	0.49	-0.01	0.40	-0.01	0.56	0.33	0.85	1									
tPh	0.07	-0.03	0.00	0.24	0.55	0.36	0.76	0.68	0.56	-0.03	0.25	-0.03	0.77	0.22	0.84	0.49	1								
hC ₄	0.12	0.11	0.13	0.42	0.77	0.42	0.74	0.57	0.33	0.11	0.51	0.00	0.41	0.39	0.64	0.8	0.34	1							
kC ₃	0.50	-0.02	0.00	0.14	0.22	0.18	0.21	0.30	0.39	-0.01	0.11	0.02	0.24	0.12	0.32	0.27	0.17	0.06	1						
kC ₇	0.50	0.82	0.89	0.70	0.18	0.32	0.09	0.15	0.53	0.78	0.63	0.25	0.16	0.60	0.12	-0.00	0.09	0.11	-0.1	1					
ω C ₂	0.51	0.05	0.01	0.11	0.14	0.11	0.17	0.23	0.44	0.04	0.11	0.02	0.15	0.07	0.28	0.23	0.16	0.03	0.95	0.02	1				
ω C ₃	0.27	0.11	0.32	0.52	0.56	0.48	0.40	0.44	0.28	0.23	0.50	0.25	0.50	0.49	0.46	0.44	0.25	0.37	0.16	0.1	0.01	1			
ω C ₄	0.37	0.10	0.35	0.64	0.74	0.63	0.58	0.66	0.22	0.20	0.46	0.15	0.65	0.63	0.55	0.57	0.34	0.51	0.16	0.17	0.01	0.8	1		
ω C ₉	0.10	-0.04	0.03	0.36	0.70	0.46	0.84	0.82	0.44	-0.01	0.22	-0.05	0.92	0.29	0.77	0.57	0.81	0.37	0.16	0.09	0.13	0.3	0.49	1	
Pyr	0.15	-0.07	0.08	0.28	0.40	0.39	0.30	0.39	0.10	0.01	0.14	0.17	0.44	0.29	0.32	0.28	0.23	0.19	0.1	-0.05	-0.06	0.6	0.58	0.3	1
Gly	0.21	0.05	0.10	0.35	0.61	0.52	0.51	0.53	0.61	0.07	0.36	0.02	0.45	0.34	0.68	0.61	0.41	0.38	0.32	0.06	0.28	0.55	0.43	0.30	0.32
MeGly	0.25	0.44	0.42	0.40	0.33	0.34	0.21	0.30	0.30	0.45	0.45	0.27	0.22	0.55	0.15	0.14	0.05	0.21	0.05	0.38	0.07	0.13	0.25	0.13	0.11

Correlation is significant at the 0.01 level (2-tailed); Above: 0.23 strong.

Correlation is significant at the 0.05 level (2-tailed); Above: 0.17 - 0.23 good.

Table 3: Results of principal component analyses (Varimax rotation with Kaiser Normalization) for concentrations of selected dicarboxylic acids, oxocarboxylic acids, pyruvic acid and α -dicarbonyls (ng/g-ice) in ice core from Gorshkov crater at UKPRF in 1697-1997.

Species	Components			
	1	2	3	4
C ₂	0.09	0.76	0.08	0.06
C ₃	-0.05	0.91	0.08	0.00
C ₄	6.38E-05	0.88	0.03	0.24
C ₅	0.41	0.74	0.03	0.39
C ₆	0.90	0.26	0.13	0.22
C ₇	0.55	0.41	0.13	0.47
C ₈	0.93	0.08	0.24	0.05
C ₉	0.84	0.25	0.03	0.29
C ₁₀	0.87	-0.06	0.26	-0.05
Ph	0.73	0.11	0.64	0.06
iPh	0.89	0.00	0.34	0.02
tPh	0.20	-0.04	0.94	0.07
ω C ₂	0.02	0.71	0.00	-0.40
ω C ₉	0.70	0.04	-0.03	0.37
Pyr	0.23	-0.02	0.11	0.78
Gly	0.53	0.13	0.70	0.12
MeGly	0.27	0.68	-0.21	-0.20

Extraction Method: Principal Component.

Rotation Method: Varimax with Kaiser.

Rotation converged in 7 iterations.

Figure Captions

Figure 1. Map showing the geographical region, where 151 meter ice core sample (ca. 301 years) was drilled in June 1998 at an ice cap on the Gorshkov crater at Ushkovsky of the Kamchatka-Peninsula, Russia, Federataion (UKPRF).

Figure 2. Average molecular distributions of diacids, ketocarboxylic and α -dicarbonyls in the Russian ice core records since 1697-1997 collected from Gorshkov crater at UKPRF.

Figure 3. Concentration changes of low molecular weight short chain dicarboxylic acids (s-DCAs), i.e (C_2 - C_5) and low molecular weight long chain dicarboxylic acids (l-DCAs) i.e (C_6 - C_{12}) in the Russian ice core records since 1697-1997 collected from Gorshkov crater at UKPRF.

Figure 4. Concentration changes of (a) - (c) branched chain saturated dicarboxylic acids (iC_4 , iC_5 and iC_6), (d) – (g) unsaturated dicarboxylic acids (M, F, mM and Ph) and (h) – (j) multifunctional diacids (hC_4 , kC_3 and kC_7) in the Russian ice core records since 1500-1997 collected from Gorshkov crater at UKPRF.

Figure 5. Concentration changes of (a-d) oxocarboxylic acids (ωC_2 - ωC_9), (e) pyruvic acid (Pyr), (f) – (g) and α -dicarbonyls (Gly and MeGly) in the Russian ice core records since 1500-1997 collected from Gorshkov crater at UKPRF.

Figure 6. Concentration ratios of five points running mean (5-RM) for (a) ωC_2 /Gly, (b) C_2 /Gly and (c) C_2 /Pyr in the Russian ice core records since 1697-1997 collected from Gorshkov crater at UKPRF.

Figure 7. Concentration changes of (a) total dicarboxylic acids (b) total ω -oxocarboxylic acids (c) total α -dicarbonyls (d) 10-year running mean of snowfall accumulation rate of hydrogen isotope ratio (δD) profile (Sato et al., 2014) in the Russian ice core records collected from Gorshkov crater at UKPRF, (e) Greenland temperature anomalies (GTA) calculated from Greenland temperature and the NH temperature (Kobashi et al., 2013), (f) reconstructed solar total irradiance since 1697-2000 [Lean, 2000] and (g) 25 years running mean (25-RM) of reconstructed PDO index since 1697-1996 [MacDonald and Case, 2005] and (h) 15-RM of multi-decadel North Atalantic oscillation reconstruction (NAO) since 1697 - 1995 [Trouet et al., 2009].

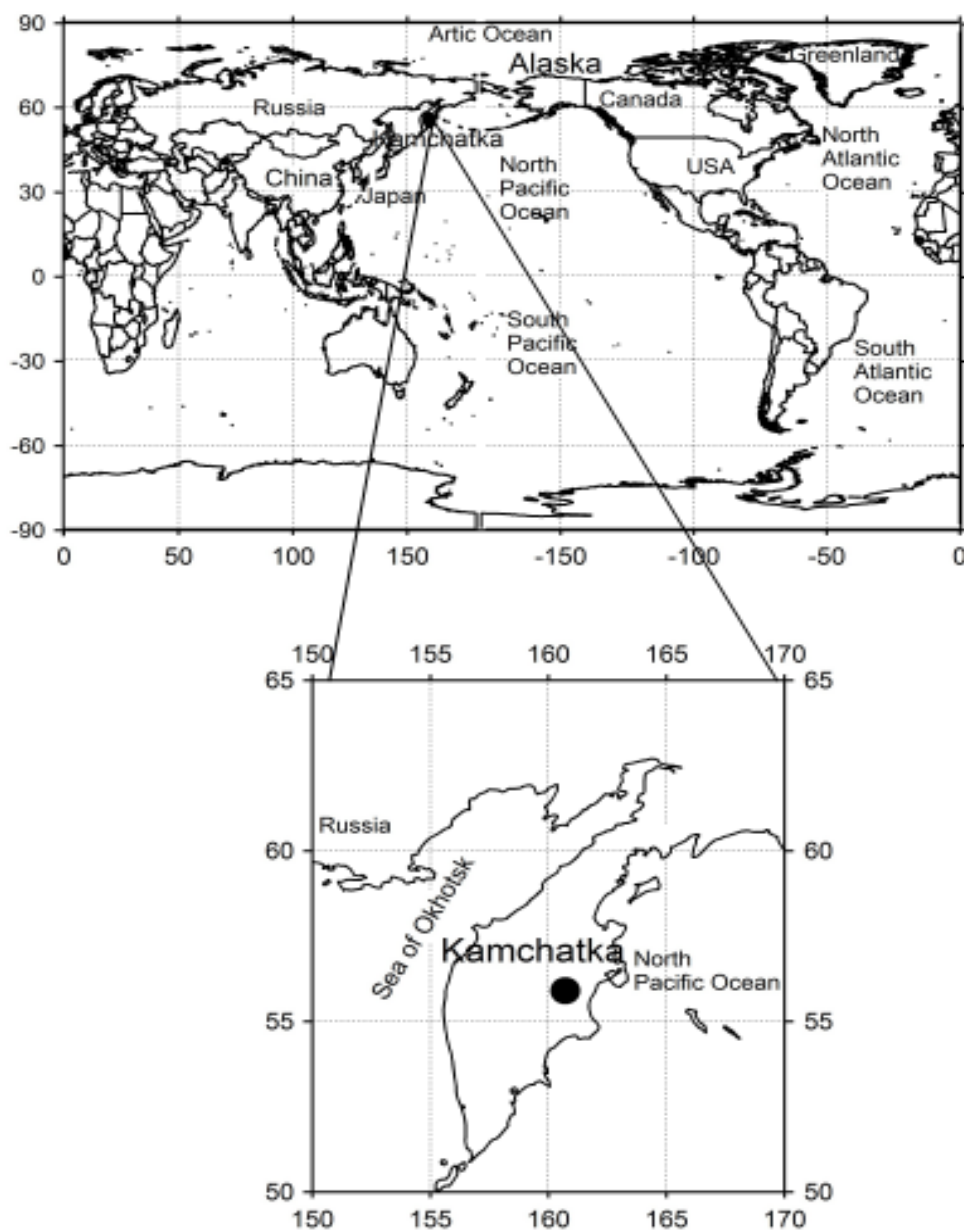


Figure 1. Map showing the geographical region, where 151 meter ice core sample (ca. 301 years) was drilled in June 1998 at an ice cap on the Gorshkov crater at Ushkovsky of the Kamchatka-Peninsula, Russian Federation (UKPRF).

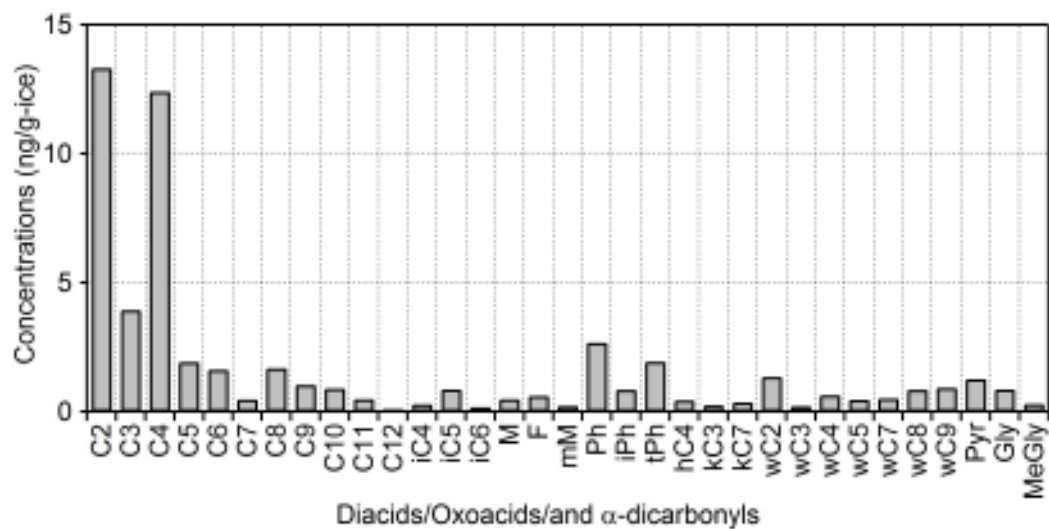


Figure 2. Average molecular distributions of diacids, oxoacids and α -dicarbonyls in the Russian ice core records since 1697-1997 collected from Gorshkov crater at UKPRF.

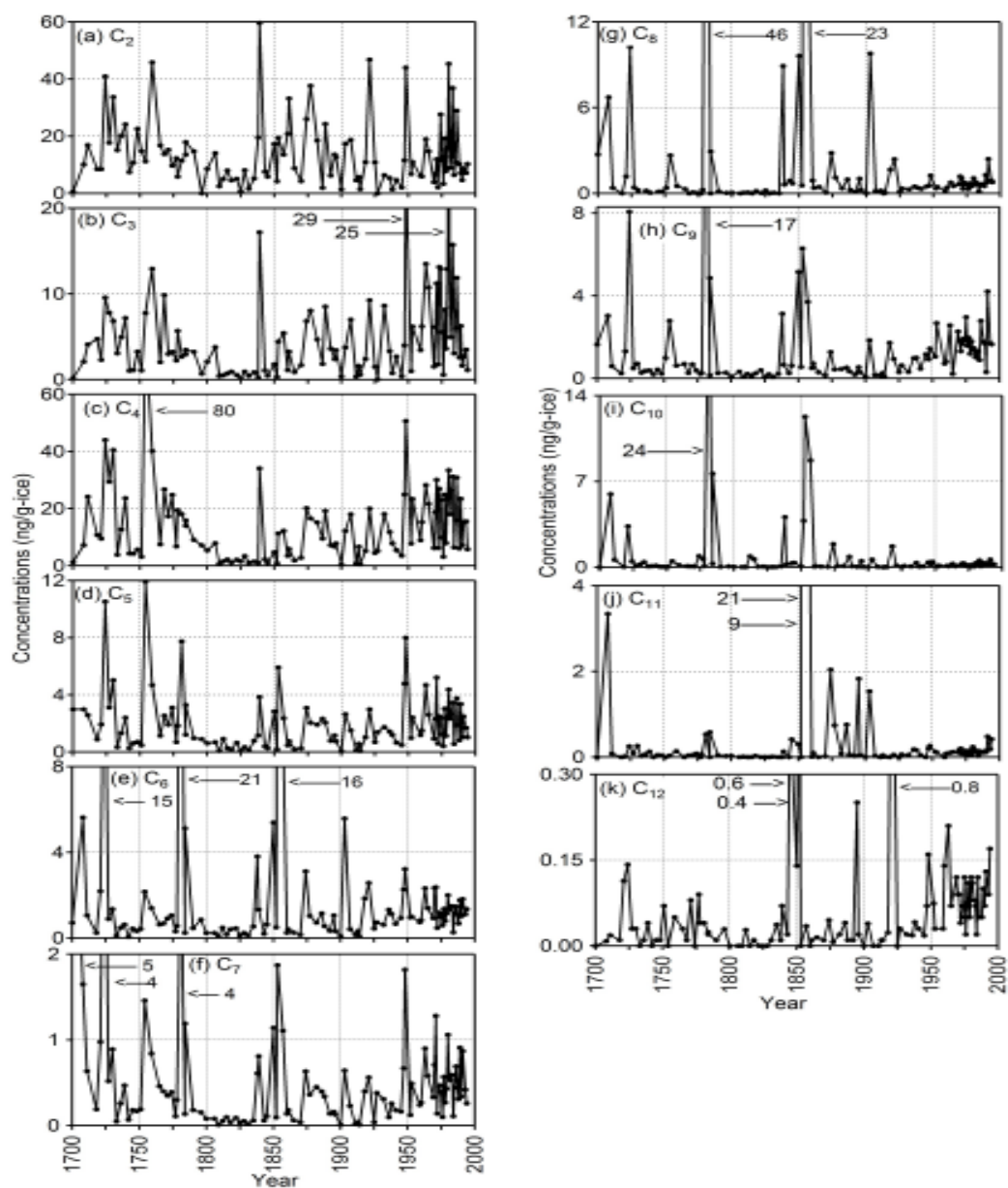


Figure 3. Concentration changes of low molecular weight short chain dicarboxylic acids (s-DCA), i.e (C_2 - C_5) and low molecular weight long chain dicarboxylic acids (l-DCA) i.e (C_6 - C_{12}) in the Russian ice core records since 1697-1997 collected from Gorshkov crater at UKPRF.

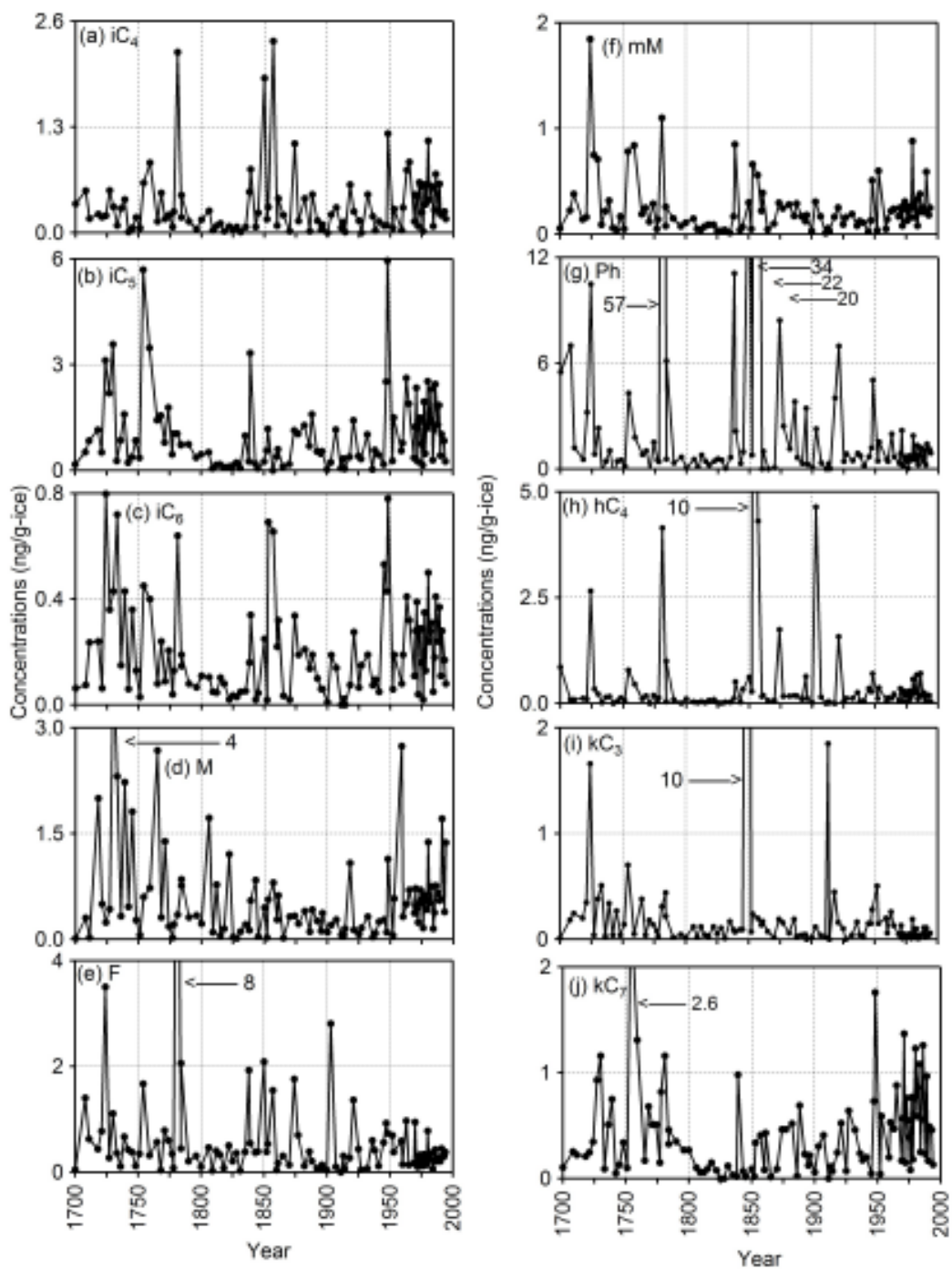


Figure 4. Concentration changes of (a) - (c) branched chain saturated dicarboxylic acids (iC_4 , iC_5 and iC_6), (d) – (g) unsaturated dicarboxylic acids (M, F, mM and Ph) and (h) – (j) multifunctional diacids (hC_4 , kC_3 and kC_7) in the Russian ice core records since 1697-1997 collected from Gorshkov crater at UKPRF.

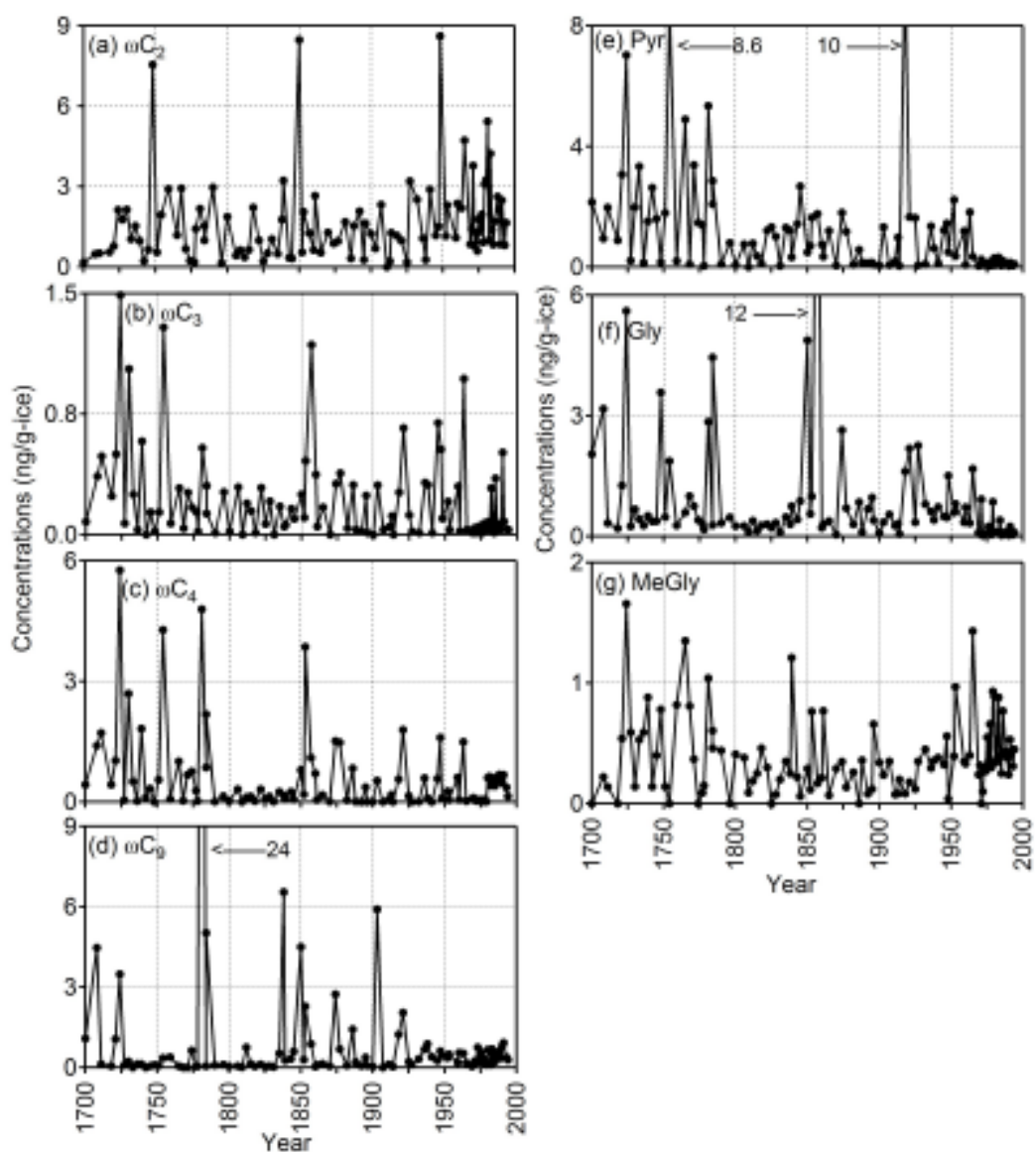


Figure 5. Concentration changes of (a) – (d) oxocarboxylic acids (ωC_2 - ωC_9), (e) pyruvic acid (Pyr) and (f) – (g) α -dicarbonyls (Gly and MeGly) in the Russian ice core records since 1697-1997 collected from Gorshkov crater at UKPRF.

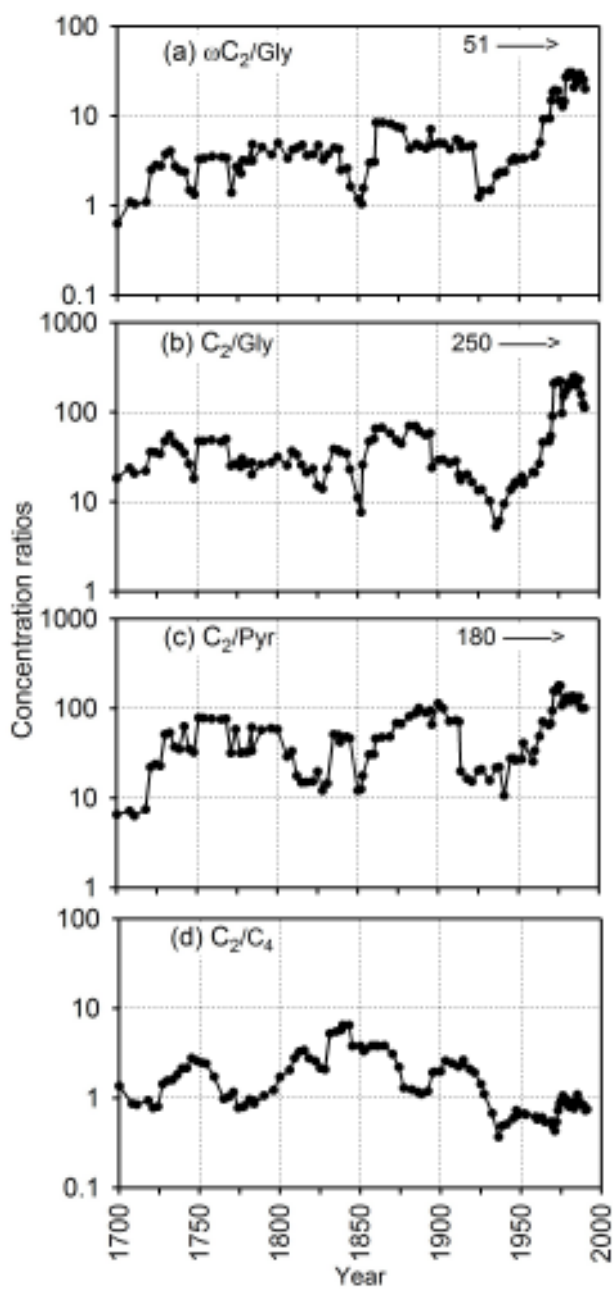


Figure 6. Concentration ratios of five points running mean (5-RM) for (a) $\omega C_2/Gly$, (b) C_2/Gly (c) C_2/Pyr and (d) C_2/C_4 in the Russian ice core records since 1697-1997 collected from Gorshkov crater at UKPRF.

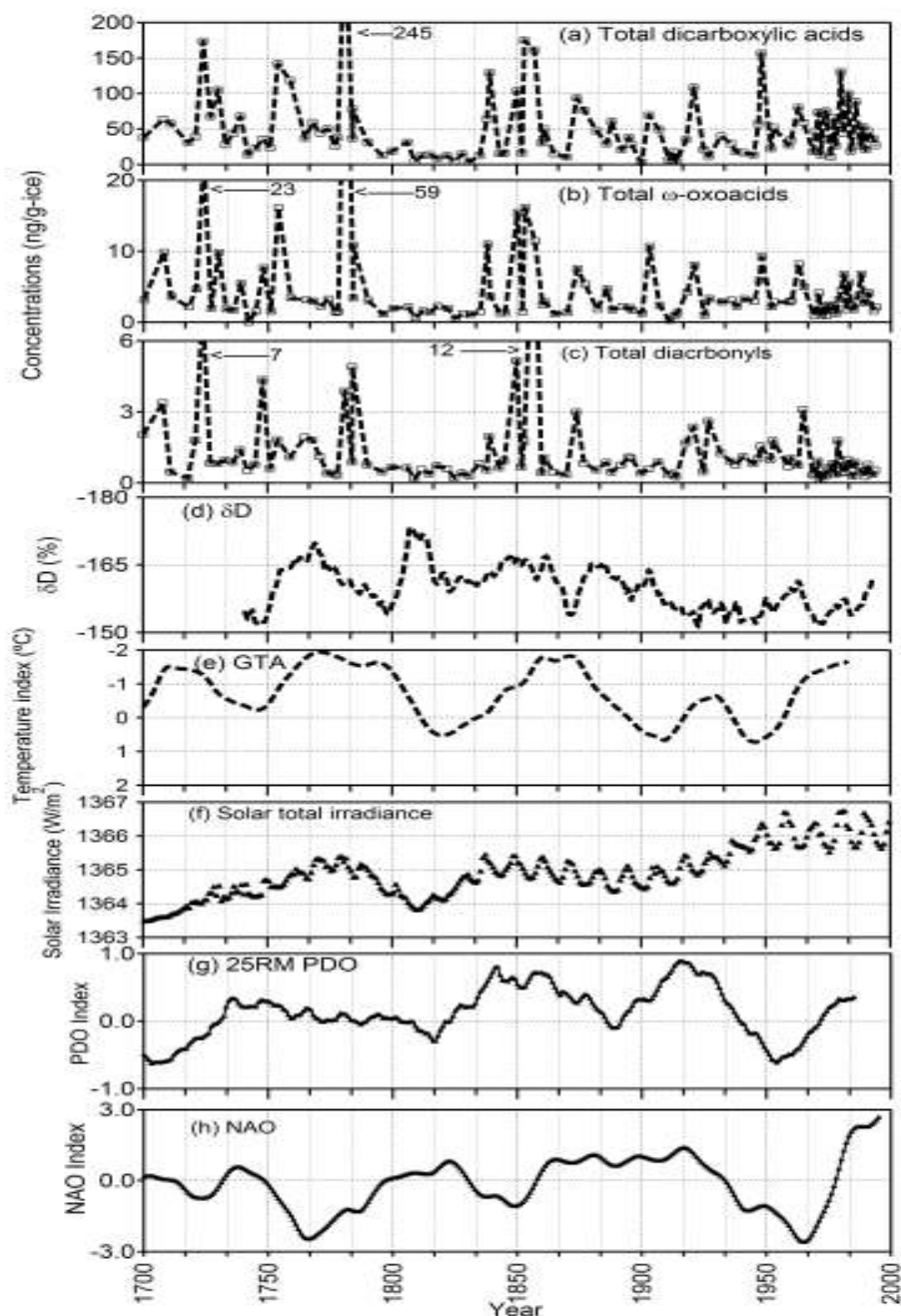


Figure 7. Concentration changes of (a) total dicarboxylic acids (b) total ω -oxocarboxylic acids (c) total α -dicarbonyls (d) 10-year running mean of snowfall accumulation rate of hydrogen isotope ratio (δD) profile [Sato *et al.*, 2014] in the Russian ice core records collected from Gorshkov crater at UKPRF, (e) Greenland Temperature Anomalies (GTA) calculated from Greenland temperature and the NH temperature [Kobashi *et al.*, 2013], (f) reconstructed solar total irradiance since 1697-2000 [Lean, 2000], (g) 25 years running mean (25-RM) of reconstructed Pacific Decadal Oscillation (PDO) since 1697-1996 [MacDonald and Case, 2005] and (h) 15-RM North Atlantic Oscillation reconstruction (NAO) since 1697 - 1995 [Trouet *et al.*, 2009].

Chapter 6: Summary and Conclusions

We found the predominance of oxalic acid followed by adipic and succinic acid for an ice core of Alaskan glacier. In addition, molecular distribution of ω -oxocarboxylic acids is characterized by the predominance of 9-oxononanoic acid followed by 4-oxobutanoic acid and glyoxylic acid. The predominance of 9-oxononanoic acid suggests that most organic species are derived from biogenic unsaturated fatty acids followed by photooxidation. Historical trends of these compounds, correlation with climate oscillation indices (e.g., North Pacific index), extra tropical Northern Hemispheric temperature index, solar total irradiance, levoglucosan and dehydroabietic acid suggest that they are produced by the oxidation of precursor compounds emitted from the biogenic and anthropogenic activities. Abrupt changes of concentrations after the 1850s suggest that the transports of organic compounds may have shifted from southeast Alaska. Historical trends of these compounds since the 1980s are controlled by similar meteorological factors, suggesting that the sea-to-air emissions of the organic precursors were associated with lower tropospheric temperature.

We found the predominance of oxalic acid, which is followed by succinic acid, and malonic acid for an ice core of Russian glacier. Similarly, molecular distribution of ω -oxocarboxylic acids is characterized by predominance of glyoxylic acid followed by 8-oxooctanoic and/or 9-oxononanoic acids. Molecular distribution from this sampling site is different than Greenland Site-J and the Aurora Peak of Alaskan ice core. Historical concentration trends of these species are fluctuated in similar ways to each other with maxima in 1725-1775, 1825-1875 and 1950s-1990s. Lower spikes reflected the

reconstructed Dalton and Damon and/or Gleissberg minima of solar irradiance, suggesting that organic compounds were strongly associated with past oxidizing capacity of the lower troposphere.

Historical concentration trends of these species and δD for the same ice core followed the Greenland Temperature Anomaly (GTA), which reflects Arctic Oscillations (AO), North Pacific Gyre Oscillation (NPGO) and/or Pacific/North American climate sensitivity (PNA) and Pacific Decadal Oscillation (PDO). These organic compounds have some link for the sea-to-air interaction, could be strongly influenced with large-scale climate changes in the North Pacific. The North Pacific ice cores are indicative of the variation of the decadal climate change in the Northern Hemisphere. Hence, this study will help to better understand the impact of climate change on oxidizing capability and sources of precursor compounds in perspective with the effect of diacid production variability and its periodic and non-periodic hind cast in the NH.

Alaskan ice core demonstrates that fatty acids are abundant in the Aurora Peak ice core (1665 - 2008) from southern Alaska. The molecular distributions of fatty acids were characterized by the predominance of $C_{16:0}$, followed by $C_{18:1}$ and $C_{14:0}$. This distribution pattern is different from that of other ice core from Greenland Site-J where longer-chain fatty acids of terrestrial higher plant origin are often more abundant. Correlation analyses of LMW fatty acids with azelaic acid, major ions, levoglucosan and sugar compounds suggest that fatty acids are mainly derived by sea-to-air emissions of phytoplankton-derived organic matter in the northern North Pacific including the Gulf of Alaska. This study further demonstrates that fatty acids are strongly associated with climate periodicity cycle, which could be transported via atmospheric circulation in the circumpolar regions.

Comparisons of fatty acid profiles in the ice core with paleoclimate proxy records such as Arctic Oscillation (AO) index and δD records in the ice core from Northeast Asia showed a strong agreement, suggesting that fatty acids in ice core can be used as useful indicators for the changes in marine biogenic inputs to Alaskan region.

Levoglucosan (ave. 543 ± 2343 ng/L), dehydroabietic (ave. 62.4 ± 97.2 ng/L) and vanillic acid (1.36 ± 3.03 ng/L) are present in the saddle of Aurora Peak, has been reported to better understand temporal trends of biomass burning activities in the source region of southern Alaska. Levoglucosan showed sporadic peaks during the 1660s-1830s, 1898, 1913, 1966 and 2005. Dehydroabietic and vanillic acid showed similar historical trends with levoglucosan at least before 1980s. Historical trends of levoglucosan, dehydroabietic acid and vanillic acid showed that biomass burning activities from resin, and lignin boreal conifer trees and other higher plant, and grasses were significant before 1830s and after 1980s in the source regions of southern Alaska. Correlation of levoglucosan with NH_4^+ ($R = 0.03$), NO_3^- (0.03), sulfate SO_4^{2-} (0.15) and NO_2^- (0.17) from the same ice core suggest that these anions and cations can not represent the gleaming signal of biomass burning activities in the source regions for the southern Alaska. These results further suggest that forest fires signal in the NH dependent on the source regions and ice core sampling sites. Hence, it inquires about the long-range and/or short-range atmospheric transport, which will be important for biomass burning tracers (i.e., levoglucosan, dehydroabietic and vanillic acid), cations and anions.

We detected interesting historical geochemical cycles of anions, i.e., nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-}) and methanesulfonate ($CH_3SO_3^-$) from 1665-2008. Concentration profiles of these anions showed unique historical trends, which are

completely different than other ice core records in the Northern and Southern Hemispheres. NO_3^- and sea salt SO_4^{2-} showed consistency in historical trends since the 1660s-1980s. CH_3SO_3^- and nss- SO_4^{2-} cycles are similar since the 1660s-1890s. Common higher spike periods for all anions (except for some points) suggest that these anions could be attributed from their same source regions, similarity of air mass chemistry, and similar effect of snowfall accumulation rate. These results further suggest that Alaskan anions could be associated with the pristine glaciochemistry rather than the contaminated atmospheric transport from the East Asian regions to the northern North Pacific. In contrast, significant impacts from human activities are recorded and concentrations are drastically increased from its background level since the 1990s, which are somewhat similar to the open ocean water of the North Pacific. Hence, this study suggests that the industrial revolution's impact is minimal in the northern North Pacific region before the 1990s.

Kamchatka ice core δD periodicity is similar to anions periodicity (except few points, e.g., 1820s and 1880s), which can further demonstrate that the North Pacific paleoclimate information is imprinted in the ice core from Alaska. Hence, multi-decadal scale atmospheric transport from middle to higher latitudes in the North Pacific is reflected as periodic cycles of NO_2^- , SO_4^{2-} and CH_3SO_3^- , which could be associated with climate oscillations, and are to be controlled as well. This agreement further suggests that Arctic Oscillation (AO), Pacific Decadal Oscillation (PDO) and/or North Pacific Gyre Oscillation (NPGO) may influence the anions periodicity cycles, which can somewhat, alter the concept of other ice core studies in the Northern and Southern Hemispheres corresponding to the anthropogenic activities.

