Title	Ice core records of biomass burning tracers (levoglucosan and dehydroabietic, vanillic and p-hydroxybenzoic acids) and total organic carbon for past 300 years in the Kamchatka Peninsula, Northeast Asia
Author(s)	Kawamura, Kimitaka; Izawa, Yusuke; Mochida, Michihiro et al.
Citation	Geochimica et Cosmochimica Acta, 99, 317-329 https://doi.org/10.1016/j.gca.2012.08.006
Issue Date	2012-12-15
Doc URL	https://hdl.handle.net/2115/50993
Type	journal article
File Information	GCA99_317-329.pdf

Revised to Geochimica Cosmochimica Acta, final version August 6, 2012

Ice core records of biomass burning tracers (levoglucosan and dehydroabietic, vanillic and *p*-hydroxybenzoic acids) and total organic carbon for past 300 years in the Kamchatka Peninsula, Northeast Asia

Kimitaka Kawamura [a,*], Yusuke Izawa [a,b], Michihiro Mochida [a,1], and Takayuki Shiraiwa [a]

[a] Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan
[b] Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810, Japan

[*] Corresponding author: Tel.: +81-11-706-5457
E-mail address: kawamura@lowtem.hokudai.ac.jp (K. Kawamura)

[1] Present address: Graduate School of Environmental Studies, Nagoya University, Nagoya 464-8601, Japan

Abstract

We successfully detected biomass burning tracers including levoglucosan and vanillic, *p*-hydroxybenzoic and dehydroabietic acids in an ice core (153 m long, ca. 300 years old) taken from Ushkovsky ice cap (altitude, 3903 m), the Kamchatka Peninsula, Northeast Asia. Concentrations of total organic carbon (TOC) were also determined in the ice core. Levoglucosan, which is produced by pyrolysis of cellulose and hemicellulose and thus is a general tracer of biomass burning, showed sporadic peaks in the years of 1705, 1759, 1883, 1915, 1949 and 1972, with the largest peak in 1949. However, its concentrations did not show a systematic increase in the last century although the concentration peaks seemingly corresponded to the higher ambient temperatures in the northern high latitudes. In contrast, dehydroabietic acid, a specific tracer of the pyrolysis of conifer resin, showed a gradual increase from the early 1900s to 1990s with a significant peak in 1970. Contributions of dehydroabietic acid to TOC also showed an increasing trend for the 20th century. Similarly, vanillic and *p*-hydroxybenzoic acids presented higher concentrations in the last half-century with sporadic peaks in 1705, 1759 and 1949. This study showed that general biomass burning tracers such as levoglucosan have been sporadically transported over the glacier of the Kamchatka Peninsula. In contrast, the ice core record of dehydroabietic acid indicated that fires of boreal conifer forest have more frequently and increasingly occurred in Far East and Siberia during the last century and transported to the Northwestern Pacific. The present study demonstrates that organic tracers of biomass burning preserved in ice core could provide historical records of biomass burning and boreal forest fires.

1. INTRODUCTION

In polar regions and high mountain areas, atmospheric chemical species are scavenged by wet (snowflakes) and dry deposition processes, and are preserved in ice sheets and snow fields, providing important information on the atmospheric composition of trace gases and aerosol particles in the past (Legrand and Mayewski, 1997). Ice core studies from polar regions often provide global information with long time scales whereas those from mid-latitudes give more information on regional environmental changes for more recent years (Schwikowski et al., 1999). Currently, organic aerosols are recognized as an important fraction of fine particles in the atmosphere (Kanakidou et al., 2005), which contains various organic components derived from anthropogenic, biogenic and photochemical sources (Simoneit, 1986; Kawamura et al., 1996). However, most ice core analyses in the previous studies are focused on inorganic species (e.g., Legrand and Mayewski, 1997) and organic species from ice core or snow have rarely been reported (Gambaro et al., 2008; Kawamura et al., 1996, 1994; Kawamura et al., 2001; Kehrwald et al., 2012; Legrand and DeAngelis, 1996; Makou et al., 2009; Nishikiori et al., 1997). Because the composition of organic aerosols can provide useful information on the source and source regions (Simoneit, 1986), the ice core studies for organic compounds are potentially important to better understand the past changes in atmospheric composition.

Biomass burning, which has a significant impact on a changing climate (Keywood et al., 2011), is an important source of organic aerosols (Simoneit, 2002). Forest fires frequently occur in many regions of the globe. Domestic burning of bio-fuels and field burning of agricultural wastes are also common in developing countries (Gustafsson et al., 2009). Large-scale forest fires emit enormous amounts of gases and carbonaceous aerosols to the atmosphere via direct vaporization/steam stripping and by thermal alteration of the organic molecules under high temperature conditions (Simoneit, 2002). The biomass burning products are long-range transported via the atmosphere to the Polar Regions and high mountains. The emissions from biomass burning are estimated to contribute up to 38% of tropospheric O_3, 39% of the particulate organic carbon, and >86% of the elemental carbon (black soot) (Fang et al., 1999; Levine et al., 1995). The majority of the total biomass burning is taking place in the tropical regions (Levine et al., 1995). In particular, the smoke pollution derived from the forest fires of Indonesia is becoming a social problem (Fang et al., 1999). Although the high latitudinal forest fires in the Northern Hemisphere contribute less than 3% of global carbon emission (Levine et al., 1995), the tropospheric chemistry of high latitudes may greatly influence the atmospheric oxidizing capacity and radiation characteristics (Browell et al., 1994; Wong and Li, 2002). The forest fire in Siberian taiga is critical because the regeneration of the damaged forest under which permafrost exists may be difficult, in contrast to the fires occurring in a tropical region. The forest fires in boreal taiga lead to the melting of permafrost under the forests and the release of methane (a strong greenhouse gas) stored under the frozen soil.

Biopolymers such as cellulose, lignin, hemicellulose, suberin, sporopollenin, chitin, etc. are the major constituents of biomass. When they are subjected to burning processes, various organic molecules are emitted to the atmosphere (Simoneit, 2002). Levoglucosan (1,6-anhydro-β-D-glucopyanose) is a major pyrolysis product (>300 °C) of cellulose and hemicellulose that typically comprise 50-70% of dry wood (Andreae and Merlet, 2001; Gao et al., 2003), although levoglucosan was detectable in lower temperature char samples (150-350 °C) with maximum yield at 250 °C (Kuo et al., 2008). This compound is emitted to the atmosphere by combustion of a woody and grassy part of biomass (Simoneit, 2002; Simoneit and Elias, 2001, 2000; Simoneit et al., 1999). Levoglucosan has been reported in the aerosol samples from urban (Fraser and Lakshmanan, 2000; Kubátová et al., 2002), remote continental (Fu et al., 2008; Gao et al., 2003) and marine sites (Fu et al., 2011; Mochida et al., 2003; Simoneit and Elias, 2000; Simoneit et al., 2004) as well as from the Arctic (Fu et al., 2009). It is also detected in lacustrine sediments from Carajas in Amazon (Elias et al., 2001) and in marine sediments from Puget Sound in Washington (Kuo et al., 2011b). Phenolic compounds such as vanillic and hydroxybenzoic acids are also emitted to the atmosphere during combustion of lignin. Lignin pyrolysis products are detected in aerosols collected from urban and rural areas (Nolte et al., 2001). Dehydroabietic acid is produced during the burning process of conifer resins (Simoneit, 2002). These biomass-burning products are predicted to be transported to the Polar Regions and stored in ice sheets. However, these biomass-burning products have never been reported in an ice core, except for vanillic acid in Greenland ice core (McConnell et al., 2007) and levoglucosan in Antarctic ice (Gambaro et al., 2008), although other organic species were reported in polar ice (Gambaro et al., 2008; Kawamura et al., 1996, 1994; Kawamura et al., 2001; Legrand and de Angelis, 1996; Makou et al., 2009; Nishikiori et al., 1997).

In this paper, we present, for the first time, a set of specific organic tracers of biomass burning in an ice core (ca. 300 years old for upper 152 m) collected from the glacier filling, Ushkovsky volcanic craters, Kamchatka Peninsula, the Russian Federation. This site is located in the outflow region of air masses from Siberia and Northeast Asia, where biomass burning and forest fires occur frequently. Here, we report ice core records of levoglucosan as well as dehydroabietic, vanillic and *p*-hydroxybenzoic acids, and discuss their historical records and variability. Although low molecular weight dicarboxylic acids including oxalic acid have been reported in biomass burning products (Narukawa et al., 1999) and reported in ice core samples (Kawamura et al., 2001; Legrand and Mayewski, 1997), they are also produced in the atmosphere by photochemical processes (Kawamura and Ikushima, 1993; Kawamura et al., 1996). Therefore, diacids cannot be considered as specific tracers of biomass burning and are not discussed here. Although we did not measure black carbon in the present study, black carbon has been studied and discussed in ice cores (e.g., Kehrwald et al., 2010; McConnell et al., 2007; Thevenon et al., 2009).

2. EXPERIMENTAL METHODS

An ice core (211.7 m long) was taken from the ice cap of Gorshkov crater at Ushkovsky volcano (56°04′N, 160°28′E, 3903 m a.s.l.) of the central part of the Kamchatka Peninsula, Russian Federation (Shiraiwa et al., 2001). The sampling site is shown in Fig.1. The ice core chronology was determined by counting the annual layers of a seasonal oxygen isotopic signal ($\delta^{18}O$) from the surface to 103.58 m in depth whereas the chronology for deeper layers was determined by using a two-dimensional thermodynamic coupled model (Salamatin et al., 2000; Shiraiwa et al., 2001). The error in the age determination of the upper 103 m was estimated to be ±2 years using four identified volcanic ash layers contained in the core (Murav'ev et al., 2007; Shiraiwa and Yamaguchi, 2002). The errors in the deeper section are considered to be larger than those of the upper 103 m. Seventy-five sections were cut off using a band saw. Ice core sections (50 cm long, 1/4 cut) were taken at every one meter for the upper 25 m and at every 4 to 5 m for the layers deeper than 25 m in depth. Approximately 1.0 cm thickness of the outer core surface was mechanically removed using a pre-cleaned ceramic knife in a cold clean room to avoid a potential contamination.

The sample sections were melted in a pre-cleaned Pyrex beaker (2 L). The samples were poisoned with $HgCl_2$ to prevent potential microbial degradation of organic compounds and stored at 4 °C in a pre-cleaned brown glass bottle (800 ml) with a Teflon-lined screw cap prior to analysis. The presence of sand layers was observed in the deeper sections (>153 m), suggesting that volcanic ash layers of snow might have melted and refrozen in the deeper layers in the past. In this study, we use 60 samples that were collected from 1.32-152.6 m in depth (1997-1693 year) and the data of deeper sections (>153 m) were not used because of the presence of many sand layers although the deeper sections were also analyzed for total organic carbon (TOC) and organic tracers.

After the homogenization (mixing) of the samples in the 800 ml glass bottle, melt water samples (80-250 ml) were transferred in a pear shape flask (300 ml) and concentrated to almost dryness using a rotary evaporator under a vacuum. The total (dissolved + particulate) organic matter in the dried samples was extracted with CH_2Cl_2/CH_3OH (2:1) mixture using ultrasonic bath. A similar extraction technique has been used to separate organic tracers present in aerosols (e.g., Simoneit et al., 2004; Fu et al., 2008). Although the biomass burning tracers are present as aerosol particles in the atmosphere, they may partition into dissolved and particulate forms when ice samples that contain aerosol particles are melted. Using the dryness and extraction technique, we can recover both the dissolved plus particulate organic matter in the melt water with reasonable recoveries as discussed later. When volcanic ash was present in the sample, the extracts were concentrated and passed through a glass column packed with quartz wool to remove the ash particles. The ash particles on the quartz wool were further eluted with CH_2Cl_2 and methanol to extract the organic compounds potentially adsorbed on the particles. The eluents were combined with the extracts. The concentrated extracts were transferred to 1.5 ml glass vial and then dried under a pure N_2 stream.

Biomass burning tracers in the extracts were derivatized with 99% N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) by heating at 70 °C for 2 h in a sealed glass vial (1.5 ml). This fraction was then dissolved in n-hexane and analyzed by gas chromatography/mass spectrometry (GC/MS): a Hewlett-Packard Model 5973 MSD coupled to a HP 6890 GC using a capillary column (HP-5MS, 30 m x 0.32 mm I.D. x 0.25 μm film thickness) installed with a split/splitless injector. The GC oven temperature was programmed from 50 °C (2 min) to 120 °C at 30 °C/min, and then to 300 °C at 6 °C/min and maintained at 300 °C for 20 min. Helium was used as a carrier gas. The mass spectrometer was operated on an electron impact mode at 70 eV. Organic compounds in the ice samples were identified by comparing the mass spectra with those of authentic standards and the mass spectral data in the NIST/Willey library. Levoglucosan, dehydroabietic acid, vanillic acid and *p*-hydroxybenzoic acid were quantified using the authentic standards as external standards (Fu et al., 2008; Simoneit et al., 2004).

Spiked experiments were conducted in triplicate to check the recoveries of target compounds during the analytical procedure. An aliquot of standard solution (10 μl) of authentic standards containing levoglucosan, dehydroabietic acid, vanillic acid and syringic acid (3.4-5.5 ng/μl each) were spiked to Milli-Q water (200 ml) placed in the pear shape flask (300 ml). The water sample was concentrated and dried by the procedure described above. The concentrates were derivatized with BSTFA and injected to GC-FID (Agilent 6890 GC) and GC/MS. The triplicate analyses of the spiked samples show that the recoveries of levoglucosan, dehydroabietic acid, vanillic acid and syringic acid were 73±10% (ave.±s.d.), 67±40%, 78±15% and 78±18%, respectively. Laboratory blanks was measured using Milli-Q water (200 ml). The results showed no detectable peaks of these compounds. Detection limits of these species were 0.003-0.005 ng/g-ice. Procedural blanks using Milli-Q water showed no detectable amounts of these compounds.

Total organic carbon (TOC) was measured by high temperature catalytic oxidation (HTCO) using a Shimadzu TOC-5000 (Sempéré and Kawamura, 1994). Aliquots of the melt water (ca. 10 ml) were taken from the 800 ml glass bottle into 20 ml glass vial and then acidified with 1.2 M HCl solution (80 µl). The samples were bubbled with ultra high purity air to remove inorganic carbon and then injected to the oxidation column maintained at 680 °C. The reported TOC data are corrected for the procedural and system blanks.

3. RESULTS AND DISCUSSION

3.1. Total organic carbon

Total organic carbon (TOC) concentrations in the ice core ranged from 410 to 2600 ng/g-ice with an average of 1200 ng/g-ice (Table 1). The averaged TOC value in the Ushkovsky ice core (elevation of site; 3903 m) is slightly lower than that (700-5700 µg/g-ice: average 1700 ng/g-ice) (Kawamura et al., 1992) reported in ice core samples collected at Site-J in Greenland (66°51.9'N, 46°15.9'W, elevation; 2030 m) and twice lower than that (290-4900 ng/g-ice: average 2300 ng/g-ice) obtained for the H-15 ice core (69°04’S, 40°46’E; elevation; 1057 m) near the coast of Antarctica (Kasukabe, 1995).

Fig. 2 gives the historical record of TOC in the Ushkovsky ice core. The TOC concentrations gradually decrease from 1700s to 1900 with peaks in 1715, 1768, 1818, 1847 and 1883. Then they fluctuate with peaks in 1928, 1949, 1966, 1975, and 1986. Although the concentrations of TOC and organic species are affected by dry deposition of atmospheric aerosols and the amounts of snowfall, these trends and fluctuations may be associated with natural variability of the emission of organic matter to the atmosphere and long-range transport to the sampling site. Interestingly, we found an abrupt increase in TOC concentrations from the late 1970s toward the early 1990s. This abrupt increase may be caused by an increased anthropogenic activity in East Asia, followed by long-range atmospheric transport to Kamchatka. The development of east Russia (e.g., Siberia and Far East) started at the beginning of the 20th century. For instance, the construction of the Siberia railroad was completed in 1905. The economic growth in east Russia and northeast China has accelerated in recent years. This suggests that an enhanced atmospheric emission of organic matter of anthropogenic origins may have begun when the industrial development started in the Siberia since the 1910s. However, such an increase in TOC has not been observed in the Site-J ice core from southern Greenland (Kawamura et al., 1992). This may be reasonable because the Ushkovsky site is much closer to the source regions in East Asia and Siberia whereas Greenland is much further away from the sources.

3.2. Biomass burning tracers

3.2.1. Levoglucosan (pyrolysis product of cellulose and hemicellulose)

Levoglucosan is a pyrolysis product of cellulose and hemicellulose (Simoneit et al., 1999), and it is also produced by combustion of lignite or brown coal (Fabbri et al., 2008; Fabbri et al., 2009; Oros and Simoneit, 2000). However, it is not produced either by hydrolysis or microbial degradation of sugar (Locker, 1988; Simoneit et al., 1999). Levoglucosan has been used as a general tracer of biomass burning in atmospheric aerosols (e.g., Fu et al., 2008; Simoneit, 2002; Simoneit et al., 1999). Although levoglucosan may not be as stable as previously thought in the atmosphere (Hoffmann et al., 2010), its concentrations are not seriously influenced during transport for several days in winter (Fraser and Lakshmanan, 2000; Hoffmann et al., 2010; Mochida et al., 2010). In the Ushkovsky ice core, levoglucosan was detected as the most abundant organic species in the total ion current (TIC) chromatogram (Fig. 3a). Fig. 3b presents the mass spectrum of levoglucosan as TMS derivative, which shows a weak molecular ion at m/z=378 and three dominant fragment ions at m/z=204, 217 and 333. Concentrations of levoglucosan ranged from less than the detection limit (0.005 ng/g-ice) to 19 ng/g-ice with an average of 0.75 ng/g-ice (Table 1).

Galactosan and mannosan are also emitted to the atmosphere as a smoke by the combustion of hemicellulose (Nolte et al., 2001; Simoneit, 2002). These anhydrosugars were detected as less abundant species than levoglucosan in the Ushkovsky ice core. Although the combustion of lignite that contains fossilized cellulose emits levoglucosan significantly, its isomers (galactosan and mannosan) are not emitted or emitted at relatively low concentrations (Fabbri et al., 2008; Fabbri et al., 2009; Kuo et al., 2011a). Thus, levoglucosan to its isomer ratios may provide a clue to differentiate the contributions of biomass and lignite burning to the ice core as discussed below.

Ice core record of levoglucosan is shown in Fig. 4a. This biomass-burning tracer showed sporadic peaks in around 1705, 1759, 1883, 1915, 1949, 1972, 1981 and 1989. These peaks may be related to enhanced forest fires on a large scale in Siberia and Far East and/or enhanced atmospheric transport of biomass and/or lignite burning plumes. These events may have been caused by forest fires in Siberia because the sampling site is located downwind of Siberia (see Fig. 1), in which boreal forest fires are frequently occurring in spring, summer and autumn (Ivanova et al., 2010). In particular, the enhanced concentration of levoglucosan in the ice core around 1949 suggest enormous fire must have occurred at around that time, although there is no reported peak of forest fires at around 1949 in the southern Siberia ice core (Eichler et al., 2011). Eichler et al. (2011) reported ice core records of K^+, NO_3^- and charcoal in southern Siberia since AD 1250 and found a high forest fire activity between AD 1600 and 1680. We could not detect any significant increase in levoglucosan concentration in the period of 1600-1680 in the Ushkovsky ice core. Further, this may suggest that the source region of the Ushkovsky ice core peak of levoglucosan is not southern Siberia, but other regions in Siberia. Interestingly, a large forest fire in Siberia was reported in 1915, which caused a significant cooling due to larger quantities of smoke particles emitted from the fire (Veltishchev et al., 1988), and the peak of levoglucosan in 1915 in the ice core (Figure 4a) matches with this event in Siberia at this time.

On the other hand, brown coal burning and subsequent transport of the plumes may be responsible to the high levels of levoglucosan. For the ice sections where high levels of levoglucosan were detected, we calculated levoglucosan/mannosan (L/M) ratios and found that L/M ratios for the annotated peaks in Figure 4a range from 3.3 to 5.0, which are much lower than those (30-90) reported for lignite burning at 200 °C (Kuo et al., 2011a) and are even lower than those (15-40, av. 21) reported for springtime Asian aerosols collected at Gosan site, South Korea (Simoneit et al., 2004). The L/M ratios (ave. 4.0) in the Ushkovsky ice core are lower than those (7.8 for winter and 6.4 for summer) for the urban aerosols from

Belgium (Pashynska et al., 2002) and those (4.7 for winter and 5.5 for summer) from Ireland (Kourtchev et al., 2011). Interestingly, the L/M ratios obtained for the ice core are typical of gymnosperm (conifer) burning (Engling et al., 2006; Fabbri et al., 2009). These comparisons suggest that lignite burning does not influence the vertical profile of levoglucosan, rather levoglucosan in the Ushkovsky ice core is most likely derived from biomass burning of conifer trees that are a major type of vegetation in Siberia.

We could not detect any clear trend of the recent increase in levoglucosan concentrations (Fig. 4a). This is in contrast to the profile of TOC, which showed a significant and gradual increase from 1970s to 1990s. However, concentrations of levoglucosan seem to increase slightly from the mid 1970s to the mid 1990s as seen in Fig. 4a. A similar weak increase was also seen for mannosan, an isomer of levoglucosan. This may suggest that contributions of biomass burning to the atmospheric aerosols have increased recently due to the frequent occurrence of boreal forest fires in Siberia (Soja et al., 2007; Valendik, 1996) and due to biomass burning of agriculture wastes in Northeast China (e.g., Fu et al., 2008; Lee et al., 2005).

In the Russian Far East area, the frequency of forest fires increased since the development by forest industry was initiated in 1930s (Sheingauz, 1998). However, such an increasing trend was not detected in the historical record of levoglucosan in the Ushkovsky ice core (Fig. 4a). This apparent mismatch may suggest a sporadically enhanced atmospheric transport of levoglucosan rather than the general increase of forest fires in the Far East. In addition, the profile of levoglucosan shows that remarkable enhancement occurred in 1705, 1759, 1883, 1915, 1949 and 1972 (Fig. 4a). Interestingly, terrestrial plant-derived biomarkers such as n-alkanes, n-alkanols and n-fatty acids showed a similar trend in the Ushkovsky ice core (Izawa, 2004). These compounds can also be emitted to the air by vaporization of leaf waxes during biomass burning processes (Nolte et al., 2001; Schauer et al., 2001). Once they are emitted to the atmosphere, they are subjected to long-range atmospheric transport by westerly winds possibly to the western North Pacific rim where Kamchatka Peninsula is located.

3.2.2. Dehydroabietic acid (pyrolysis product of conifer resin)

In the Ushkovsky ice core, we also detected dehydroabietic acid, which is another tracer of biomass burning. This acid is produced by pyrolytic dehydration of abietic acid, which is a principal component of conifer resin (Simoneit et al., 1993). Hence, dehydroabietic acid can be used as a more specific tracer of the burning of conifer trees. The concentrations of dehydroabietic acid ranged from below detection limit (0.003 ng/g-ice) to 0.47 ng/g-ice with average of 0.054 ng/g-ice (Table 1). Its average concentration is ca. 14 times lower than that (0.75 ng/g-ice) of levoglucosan, which is a general tracer of biomass burning.

Fig. 4b presents historical record of dehydroabietic acid in Ushkovsky ice core. We found a gradual increase in the concentration of dehydroabietic acid from the mid 1900s to the 1990s (Fig. 4b). It is of interest to note that levoglucosan did not show such an increase in the last century, although a weak increase was obtained for the last 30 years (Fig. 4a). Such an increase of dehydroabietic acid demonstrates that the burning of pine trees in Siberia is more frequently occurring and/or the burning plumes are more frequently transported to the sampling site in those years. More frequent forest fires in the boreal forest may have been caused as a result of recent global warming and drier conditions associated with the global change (Soja et al., 2007). The dominant vegetations of boreal forest in Siberia are characterized by larch, pine, spruce and fir (Ivanova et al., 2010). Dehydroabietic acid did not show a peak in the years when levoglucosan showed sporadic peaks although a simultaneous peak was observed in 1949 for two biomass burning tracers (Fig. 4a). For example, dehydroabietic acid showed a very strong peak in 1970/1971when levoglucosan did not show a peak (Fig. 4a). This strong peak should suggest that biomass burning plumes from boreal conifer forests probably in Siberia were transported over the Kamchatka Peninsula because air masses can be often transported from Siberia to the Northwestern Pacific rim as discussed in section 3.4.

The apparent discrepancy between two biomass-burning tracers may suggest that levoglucosan probably did not originate from the boreal forest fires in Siberia where pine trees are common, whereas dehydroabietic acid was most likely derived from the boreal forest fires in Siberia. One possible explanation is that levoglucosan could have been transported from other regions further south including mid-latitudes in East Asia where broad-leaf trees are common. However, this interpretation seems to conflict with the lower L/M ratios (ave. 4.0) that suggests gymnosperm sources for anhydrosugars as discussed above. If the burning of deciduous forests of the south were a significant source to the ice core, the L/M ratios should have been much higher. Alternatively, dehydroabietic acid may have been in part decomposed during long-range atmospheric transport because aromatic structure of the compound is relatively unstable compared to levoglucosan due to the higher sensitivity to photodegradation (Shakya et al., 2011; Simoneit, 2002; Simoneit and Elias, 2001). If dehydroabietic acid were significantly decomposed in the atmosphere during long-distance transport prior to arriving and scavenging over the ice sheet, the significance of conifer burning in Siberia should have been more intensive in these days (see Fig. 4b).

3.2.3. Vanillic and *p*-hydroxybenzoic acids (pyrolysis products of lignin)

Vanillic acid and *p*-hydroxybenzoic acid are produced by incomplete combustion of conifers and grasses, respectively (Simoneit, 2002; Simoneit et al., 1993). Vanillic acid and *p*-hydroxybenzoic acids, which have been used as biomass-burning tracers of lignin (Simoneit, 2002), were detected in the Ushkovsky ice core. Mass spectra of TMS derivative of vanillic acid are characterized by specific fragment ions at m/z=223, 267 and 297 and a molecular ion of m/z=312 (see Fig. 3c). Concentrations of vanillic acid ranged from below detection limit (0.005 ng/g-ice) to 0.13 ng/g-ice with an average of 0.015 ng/g-ice (Table 1). Its average concentration is ca. 56 times lower than that of levoglucosan and 4 times lower than that of dehydroabietic acid. Mass spectra of *p*-hydroxybenzoic acid gave specific mass fragments at m/z=193, 223 and 267 and molecular ion at m/z=282 (Fig. 3d). The concentrations of *p*-hydroxybenzoic acid ranged from below detection limit (0.005 ng/g-ice) to 1.74 ng/g-ice with an average of 0.24 ng/g-ice (Table 1). The average concentration of *p*-hydroxybenzoic acid is about 4 times lower than levoglucosan, but about 4 times higher than that of dehydroabietic acid and 16 times higher than that of vanillic acid.

Vertical profiles of vanillic acid showed sporadic peaks in 1705, 1759, 1949, 1971 and 1992 (Fig. 4c) whereas *p*-hydroxybenzoic acid showed peaks at 1705, 1759,1883, 1915, 1949, 1972, 1984 and 1992 (Fig. 4d). The major peaks of these tracers are consistent with those of levoglucosan (see Fig. 4a), suggesting that these three tracers are emitted from similar combustion sources and source regions. The covariance of these biomass-burning tracers demonstrates that the biomass burning plumes of lignin and cellulose are transported over long distances to the glaciers of the Kamchatka Peninsula, although they may potentially be subjected to OH radical attack during this transport (Hennigan et al., 2010; Hoffmann et al., 2010; Kessler et al., 2010). The similarity in the ice core profiles among the biomass burning tracers (levoglucosan, vanillic acid and *p*-hydroxybenzoic acid) is reasonable because these components are both present in the woody parts of trees. It is of interest to note that these peaks obtained for levoglucosan and two lignin tracers (vanillic and *p*-hydroxybenzoic acids) were not observed in the profile of dehydroabietic acid, except for the peak of 1949 (Fig. 4b).

The different behavior of biomass burning tracer of conifer (dehydroabietic acid) than those of lignin and cellulose suggests that biomass burning plumes with different sources and source regions were delivered to the sampling site. Because dehydroabietic acid is produced by the pyrolysis of resins that are present on the bark surfaces and needle leaves in addition to woody tissues of conifers, its emission by burning process may be different from those of lignin and cellulose, which are located in the woody part. The lack of covariance between resin and lignin/cellulose burning tracers may suggest that the tree barks and needle leaves that contain abundant resin components in the boreal conifer are easily burned to result in the emission of dehydroabietic acid to the atmosphere but the burning of woody parts may be restricted leaving the unburned conifer trees stand. This kind of burning situation of the conifer trees has been often reported in Siberia (Eichler et al., 2011) .

3.3. Relative concentrations of levoglucosan and other key biomass burning tracers in ice core and ambient aerosols

Simoneit and his colleagues reported relative concentrations of levoglucosan, dehydroabietic acid and vanillic acid in ambient aerosols from various locations (Simoneit et al., 1999). For winter (mostly December) aerosols, levoglucosan/dehydroabietic acid/vanillic acid ratios were reported to be 100/17/2 for the 1985 Corvallis aerosols from Oregon, 100/14/2 for the 1989 Pasadena aerosols from southern California, and 100/6/1.2 for the 1995 Fresno aerosols from northern California. These comparisons indicate that dehydroabietic acid, a specific tracer of burning of conifer resin, is more enriched in the northern aerosols from Oregon. In Oregon, conifer trees may be more frequently used in wood stoves during winter for house heating compared to broad-leaf trees. Interestingly, the average ratios (100/20/6) calculated for the Ushkovsky ice core (1953-1996) were similar with those of the ambient aerosols from Oregon, although the relative abundances of dehydroabietic acid and vanillic acid were higher in the ice core. The higher relative abundances of these acids in the ice may be involved with their source regions in Siberia where conifer trees are dominant species of vegetation.

3.4. Source regions of biomass burning tracers in the Ushkovsky ice core

To better understand the source regions of biomass burning tracers detected in the Ushkovsky ice core, we conducted 7 days backward air mass trajectory analyses at the Ushkovsky ice core-sampling site for four seasons in 2001 using the HYSPLIT model of the National Oceanic and Atmospheric Administration (http://www.ready.noaa.gov/ready/open/hysplit4.html) (Draxler and Hess, 1997; Draxler and Hess, 1998).

As shown in Fig. 5, the trajectory analyses for different seasons showed that the air mass source regions are mainly Siberia, Far East, North China and Eastern Europe as well as the western Northern North Pacific. These regions, in particular Siberia, are known as areas where forest fires occur frequently (Soja et al., 2007). The aerosols containing the biomass burning products have been transported over the sampling site of Kamchatka Peninsula through the atmosphere and deposited over the glacier by wet and dry processes. However, the trajectory analyses showed that there is no significant air mass contribution from Alaska and North America to the Ushkovsky site (Fig. 5). The backward air mass trajectory analyses suggest that the main source regions of biomass burning tracers detected in the Ushkovsky ice core are located in between Europe and Russia within the latitude band of 40-70 °N (see Fig.

5). The biomass burning tracers emitted from these regions may be transported to the Kamchatka Peninsula by the westerly winds.

Fig. 6 shows an estimated annual emission of total particular matter (TPM) from fires in the Northern Hemisphere for the year of 2001. The original data were taken from Global Fire Emission Database version 2.1 (GFEDv2.1) (http://daac.ornl.gov/VEGETATION/guides/global_fire_emissions_v2.1.html) (Randerson et al., 2007; van der Werf et al., 2006). Fire emissions of TPM can been seen to be high in western to eastern Russia with the latitude band of 50-60°N and in the northeast Siberia with the latitude band of 60-70°N. A similar emission map was obtained for 2002 (results are not shown as a figure). These areas are the source regions of air masses transported to the Ushkovsky ice cap (see Fig. 5). Thus, the biomass burning tracers detected in the ice core samples could have been transported in the atmosphere from the Russian regions. It is reasonable because the westerly winds are dominant in Northeast Asia. Although Southeast Asia and central Africa are important source regions of fire-emitted TPM (Fig. 6), these regions may not have contributed to the biomass burning tracers detected in the Ushkovsky ice core because air mass trajectories do not support an atmospheric transport from such regions (Fig. 5).

However, the above interpretations based on current fire emission inventories and air mass trajectories may not be applicable because we do not understand the past air circulation patterns that may have transported the biomass burning plumes from the Southeast Asian regions to the Kamchatka Peninsula in the Northeastern Pacific in the last few centuries. In fact, we found that the peaks of levoglucosan (Fig. 4a) correspond to higher ambient temperatures reconstructed in the northern North Hemisphere based on tree rings (Jacoby and Darrigo, 1989). This correlation suggests a possibility that the strong peaks of levoglucosan detected in the Ushkovsky ice core may have been involved with enhanced transport of biomass burning plumes originated from the low and mid latitudes including Southeast Asia when the Arctic air temperature increased. This hypothesis on the meridional transport of biomass burning plumes from tropics to the high latitudes associated with the Arctic warming needs to be verified by future studies.

4. CONCLUSIONS

The present study reported, for the first time, the historical records of biomass burning–derived organic tracers such as levoglucosan and dehydroabietic, vanillic and *p*-hydroxybenzoic acids in the Ushkovsky ice core, Kamchatka Peninsula, Russia. Although levoglucosan, the most abundant biomass-burning tracer in the ice core, showed sporadic peaks, there is no clear increase in the concentrations toward the present. Because levoglucosan is a general tracer of pyrolysis of cellulose, its sporadic peaks suggest that large-scale forest fires may have occurred in Siberia, Far East, Northeast Asia and Southeast Asia in the past. In contrast, concentrations of dehydroabietic acid, which is a specific tracer of pyrolysis of conifer resin, showed a gradual increase from the early 1900s to the present. This historical increase suggests that burning of boreal forests, characterized by conifer trees, has been enhanced significantly during the last one hundred years. This ice core record is consistent with the records of the forest fires and burned forest areas in Siberia (Soja et al., 2007). The present study demonstrated that organic tracers of biomass burning preserved in ice core are useful to reconstruct the historical records of biomass burning and forest fires on a local and regional scale.

ACKNOWLEDGEMENTS

This study was partly supported by a Grant-in-aid No. 14204055 from the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Science, Sport and Culture, Japan. We appreciate the provision of HYSPLIT transport model by the NOAA Air Resources Laboratory (ARL) and two anonymous reviewers for their critical and helpful comments. We also thank P. Fu for his helpful comments, K. Ono for her technical assistance of GC/MS data analyses for galactosan and mannosan, and O. Seki for his useful suggestion.

REFERENCES

Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. Global Biogeochem. Cycles 15, 955-966.

Browell, E.V., Fenn, M.A., Butler, C.F., Grant, W.B., Harriss, R.C., Dhipham, M.C., 1994. Ozone and aerosol distributions in the summertime troposphere over Canada. J. Geophys. Res. 99, 1739-1755.

Draxler, R.R., Hess, G.D., 1997. Description of the HYSPLIT_4 Modeling System. NOAA Technical Memorandum ERL ARL-224.

Draxler, R.R., Hess, G.D., 1998. An overview of the HYSPLIT_4 modelling system for trajectories, dispersion and deposition. Australian Meteorological Magazine 47, 295-308.

Eichler, A., Tinner, W., Brutsch, S., S., O., T., P., Schwikowski, M., 2011. An ice-core based history of Siberian forest fires since AD 1250. Quaternary Science Reviews 30, 1027-1034.

Elias, V.O., Simoneit, B.R.T., Cordeiro, R.C., Turcq, B., 2001. Evaluating levoglucosan as an indicator of biomass burning in Carajás, Amazônia: A comparison to the charcoal record. Geochim. Cosmochim. Acta 65, 267-272.

Engling, G., Carrico, C.M., Kreldenweis, S.M., Collett, J.L., Day, D.E., Malm, W.C., Lincoln, E., Hao, W.M., Iinuma, Y., Herrmann, H., 2006. Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection. Atmos Environ 40, S299-S311.

Fabbri, D., Marynowski, L., Fabianska, M.J., Zaton, M., Simoneit, B.R.T., 2008. Levoglucosan and other cellulose markers in pyrolysates of miocene lignites: Geochemical and environmental implications. Environ Sci Technol 42, 2957-2963.

Fabbri, D., Torri, C., Simonei, B.R.T., Marynowski, L., Rushdi, A.I., Fabianska, M.J., 2009. Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites. Atmos Environ 43, 2286-2295.

Fang, M., Zheng, M., Wang, F., To, K.L., Jaafar, A.B., Tong, S.L., 1999. The solvent-extractable organic compounds in the Indonesia biomass burning aerosols – characterization studies. Atmos. Environ. 33, 783-795.

Fraser, M.P., Lakshmanan, K., 2000. Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols. Environ. Sci. Technol. 34, 4560-4564.

Fu, P.Q., Kawamura, K., Okuzawa, K., Aggarwal, S.G., Wang, G., Kanaya, Y., Wang, Z., 2008. Organic molecular compositions and temporal variations of summertime mountain aerosols over Mt. Tai, North China Plain. J. Geophys. Res., [Atmos] 113, D19107, doi:10.1029/2008JD009900.

Fu, P.Q., Kawamura, K., Barrie, L.A., 2009. Photochemical and other sources of organic compounds in the Canadian high Arctic aerosol pollution during winter-spring. Environ. Sci. Technol. 43, 286-292.

Fu, P.Q., Kawamura, K., Miura, K., 2011. Molecular characterization of marine organic aerosols collected during a round-the-world cruise. J Geophys Res-Atmos 116, doi:10.1029/2011jd015604.

Gambaro, A., Zangrando, R., Gabrielli, P., Barbante, C., Cescon, P., 2008. Direct determination of levoglucosan at the picogram per milliliter level in Antarctic ice by high-performance liquid chromatography/electrospray ionization triple quadrupole mass spectrometry. Analytical Chemistry 80, 1649-1655.

Gao, S., Hegg, D.A., Hobbs, P.V., Kirchstetter, T.W., Magi, B.I., Sadilek, M., 2003. Water-soluble organic compounds in aerosols associated with Savanna fires in southern Africa: Identification, evolution, and distribution. J. Geophys. Res. 108, 8491, doi:8410.1029/2002JD002324.

Gustafsson, Ö., Kruså, M., Zencak, Z., Sheesley, R.J., Granat, L., Engström, E., Praveen, P.S., Rao, P.S.P., Leck, C., Rodhe, H., 2009. Brown clouds over South Asia: Biomass or fossil fuel combustion? Science 323, 495-498.

Hennigan, C.J., Sullivan, A.P., Collett Jr, J.L., Robinson, A.L., 2010. Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. Geophys. Res. Lett. 37, doi:10.1029/2010GL043088.

Hoffmann, D., Tilgner, A., Iinuma, Y., Herrmann, H., 2010. Atmospheric stability of levoglucosan: a detailed laboratory and modeling study. Environ. Sci. Technol. 44, 694-699.

Ivanova, G.A., Ivanov, V.A., Kukavskaya, E.A., Soja, A.J., 2010. The frequency of forest fires in Scots pine stands of Tuva, Russia. Environmental Research Letters 5, 10.1088/1748-9326/1085/1081/015002.

Izawa, Y., 2004. Changes in the atmospheric environments reconstructed from the Ushkovsky ice core taken from the Kamchatka Peninsula for the last 300 years. A thesis for Master's degree, Hokkaido University, pp.71.

Jacoby, G.C., Darrigo, R., 1989. Reconstructed Northern Hemisphere Annual Temperature since 1671 Based on High-Latitude Tree-Ring Data from North-America. Climatic Change 14, 39-59.

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modelling: a review. Atmos. Chem. Phys. 5, 1053-1123.

Kasukabe, H., 1995. Geochemical studies of low molecular weight dicarboxylic acids and related compounds in the Arctic aerosols and an ice core from Antarctic, Tokyo Metropolitan University, Tokyo.

Kawamura, K., Yokoyama, K., Fujii, Y., 1992. Vertical profiles of total organic carbon and polar organic compounds in the ice core from Site-J, Greenland. Proc. of the NIPR Symp. on Polar Meteorol. and Glaciol. 6, 99-105.

Kawamura, K., Ikushima, K., 1993. Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere. Environ. Sci. Technol. 27, 2227-2235.

Kawamura, K., Suzuki, I., Fujii, Y., Watanabe, O., 1994. Ice Core Record of Polycyclic Aromatic-Hydrocarbons over the Past 400 Years. Naturwissenschaften 81, 502-505.

Kawamura, K., Suzuki, I., Fujii, Y., Watanabe, O., 1996. Ice core record of fatty acids over the past 450 years in Greenland. Geophys. Res. Lett. 23, 2665-2668.

Kawamura, K., Yokoyama, K., Fujii, Y., Watanabe, O., 2001. A Greenland ice core record of low molecular weight dicarboxylic acids, ketocarboxylic acids, and alpha-dicarbonyls: A trend from Little Ice Age to the present (1540 to 1989 AD). J. Geophys. Res., [Atmos] 106, 1331-1345.

Kehrwald, N., Zangrando, R., Gambaro, A., Barbante, C., 2010. Fire and climate: Biomass burning recorded in ice and lake cores. EPJ Web of Conferences 9, 105-114.

Kehrwald, N., Zangrando, R., Gabrielli, P., Jaffrezo, J.L., Boutron, C., Barbante, C., Gambaro, A., 2012. Levoglucosan as a specific marker of fire events in Greenland snow. Tellus B 64.

Kessler, S.H., Smith, J.D., Che, D.L., Worsnop, D.R., Wilson, K.R., Kroll, J.H., 2010. Chemical Sinks of Organic Aerosol: Kinetics and Products of the Heterogeneous Oxidation of Erythritol and Levoglucosan. Environ Sci Technol 44, 7005-7010.

Keywood, M., Kanakidou, M., Stohl, A., Dentener, F., Grassi, G., Meyer, C.P., Torseth, K., Edwards, D., Thompson, A.M., Lohmann, U., Burrows, J., 2011. Fire in the Air: Biomass burning impacts in a changing climate. Critical Reviews in Environmental Science and Technology, doi: 10.1080/10643389.10642011.10604248.

Kourtchev, I., Hellebust, S., Bell, J.M., O'Connor, I.P., Healy, R.M., Allanic, A., Healy, D., Wenger, J.C., Sodeau, J.R., 2011. The use of polar organic compounds to estimate the contribution of domestic solid fuel combustion and biogenic sources to ambient levels of organic carbon and PM(2.5) in Cork Harbour, Ireland. Science of the Total Environment 409, 2143-2155.

Kubátová, A., Vermeylen, R., Claeys, M., Cafmeyer, J., Maenhaut, W., 2002. Organic compounds in urban aerosols from Gent, Belgium: Characterization, sources, and seasonal differences. J. Geophys. Res., [Atmos] 107, D21, 8343, doi:8310.1029/2001JD000556.

Kuo, L.J., Herbert, B.E., Louchouarn, P., 2008. Can levoglucosan be used to characterize and quantify char/charcoal black carbon in environmental media? Organic Geochemistry 39, 1466-1478.

Kuo, L.J., Louchouarn, P., Herbert, B.E., 2011a. Influence of combustion conditions on yields of solvent-extractable anhydrosugars and lignin phenols in chars: Implications for characterizations of biomass combustion residues. Chemosphere 85, 797-805.

Kuo, L.J., Louchouarn, P., Herbert, B.E., Brandenberger, J.M., Wade, T.L., Crecelius, E., 2011b. Combustion-derived substances in deep basins of Puget Sound: Historical inputs from fossil fuel and biomass combustion. Environmental Pollution 159, 983-990.

Lee, B.C., Shimizu, Y., Matsuda, T., Matsui, S., 2005. Characterization of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in deposited road particles (DRPs) from Lake Biwa area, Japan. Environ Sci Technol 39, 7402-7409.

Legrand, M., de Angelis, M., 1996. Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone. J Geophys Res-Atmos 101, 4129-4145.

Legrand, M., DeAngelis, M., 1996. Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone. J Geophys Res-Atmos 101, 4129-4145.

Legrand, M., Mayewski, P., 1997. Glaciochemistry of polar ice cores: A review. Reviews of Geophysics 35, 219-243.

Levine, J.S., Cofer, W.R., Cahoon, J.A.R., Winstead, E.L., 1995. Biomass burning: a driver for global change. Environ. Sci. Technol. 29, 120A-125A.

Locker, H.B., 1988. The use of levoglucosan to assess the environmental impact of residential wood-burning on air quality. Ph. D. thesis, Dartmouth College, Hanover, NH, 137.

Makou, M.C., Thompson, L.G., Montlucon, D.B., Eglinton, T.I., 2009. High-sensitivity measurement of diverse vascular plant-derived biomarkers in high-altitude ice cores. Geophys Res Lett 36, L13501, doi:13510.11029/12009GL037643.

McConnell, J.R., Edwards, R., Kok, G.L., Flanner, M.G., Zender, C.S., Saltzman, E.S., Banta, J.R., Pasteris, D.R., Carter, M.M., Kahl, J.D.W., 2007. 20th-century industrial black carbon emissions altered arctic climate forcing. Science 317, 1381-1384.

Mochida, M., Kawamura, K., Umemoto, N., Kobayashi, M., Matsunaga, S., Lim, H.J., Turpin, B.J., Bates, T.S., Simoneit, B.R.T., 2003. Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: Continental outflow of organic aerosols during the ACE-Asia campaign. J. Geophys. Res., [Atmos] 108, D23, 8638, doi:10.1029/2002JD003249.

Mochida, M., Kawamura, K., Fu, P., Takemura, T., 2010. Seasonal variation of levoglucosan in aerosols over the western North Pacific and its assessment as a biomass-burning tracer. Atmos. Environ. 44, 3511-3518.

Murav'ev, Y.D., Ovsyannikov, A.A., Shiraiwa, T., 2007. Activity of the Northern Volcano Group According to Drilling Data in the Ushkovsky Crater Glacier, Kamchatka. Journal of Volcanology and Seismology 1, 42-52.

Narukawa, M., Kawamura, K., Takeuchi, N., Nakajima, T., 1999. Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires. Geophys. Res. Lett. 26, 3101-3104.

Nishikiori, M., Kawamura, K., Fujii, Y., 1997. Distribution and historical records of aliphatic carboxylic acids in the H15 ice core from Antarctica. Proc. NIPR Symp. Polar Meteorol. Glaciol. 11, 76-86.

Nolte, C.G., Schauer, J.J., Cass, G.R., Simoneit, B.R.T., 2001. Highly polar organic compounds present in wood smoke and in the ambient atmosphere. Environ. Sci. Technol. 35, 1912-1919.

Oros, D.R., Simoneit, B.R.T., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. Fuel 79, 515-536.

Pashynska, V., Vermeylen, R., Vas, G., Maenhaut, W., Claeys, M., 2002. Development of a gas chromatographic/ion trap mass spectrometric method for the determination of levoglucosan and saccharidic compounds in atmospheric aerosols. Application to urban aerosol. J. Mass Spectrom. 37, 1249-1257.

Randerson, J.T., van der Werf, G.R., Giglio, L., Collatz, G.J., Kasibhatla, P.S., 2007. Global Fire Emissions Database, Version 2 (GFEDv2.1). Data set. Available on-line [http://daac.ornl.gov/] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A. doi:10.3334/ORNLDAAC/849.

Salamatin, A.N., Murav'yev, Y.D., Shiraiwa, T., Matsuoka, K., 2000. Modelling dynamics of glaciers in volcanic craters. Journal of Glaciology 46, 177-187.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2001. Measurement of emissions from air pollution sources. 3. C_1-C_{29} organic compounds from fireplace combustion of wood. Environ. Sci. Technol. 35, 1716-1728.

Schwikowski, M., BrÜtsch, S., Gäggeler, H.W., Schotterer, U., 1999. A high-resolution air chemistry record from an Alpine ice core: Fiescherhorn glacier, Swiss Alps. J. Geopys. Res. 104, 13709-13719.

Sempéré, R., Kawamura, K., 1994. Comparative distributions of dicarboxylic-acids and related polar compounds in snow rain and aerosols from urban atmosphere. Atmos Environ 28, 449-459.

Shakya, K.M., Louchouarn, P., Griffin, R.J., 2011. Lignin-Derived Phenols in Houston Aerosols: Implications for Natural Background Sources. Environ Sci Technol 45, 8268-8275.

Sheingauz, A., 1998. Forest fire in Primorskiy and Khabarovskiy Krais, Their causes and consequences. Unpublished report prepared for Institute of Global Environmental Strategies (IGES).

Shiraiwa, T., Murav'yev, Y.D., Kameda, T., Nishio, F., Toyama, Y., Takahashi, A., Ovsyannikov, A.A., Salamatin, A.N., Yamagata, K., 2001. Characteristics of a crater glacier at Ushkovsky volcano, Kamchatka, Russia, as revealed by the physical properties of ice cores and borehole thermometry. Journal of Glaciology 47, 423-432.

Shiraiwa, T., Yamaguchi, S., 2002. Reconstruction of glacier mass balance and climate changes in the Kamchatka Peninsula. J. Geography 111, 476-485.

Simoneit, B.R.T., 1986. Characterization of organic constituents in aerosols in relation to their origin and transport. Int. J. Environ. Anal. Chem. 23, 207-237.

Simoneit, B.R.T., Rogge, W.F., Mazurek, M.A., Standley, L.J., Hildemann, L.M., Cass, G.R., 1993. Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion. Environ. Sci. Technol. 27, 2533-2541.

Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmos. Environ. 33, 173-182.

Simoneit, B.R.T., Elias, V.O., 2000. Organic tracers from biomass burning in atmospheric particulate matter over the ocean. Mar. Chem. 69, 301-312.

Simoneit, B.R.T., Elias, V.O., 2001. Detecting organic tracers from biomass burning in the atmosphere. Mar. Pollut. Bull. 42, 805-810.

Simoneit, B.R.T., 2002. Biomass burning-a review of organic tracers for smoke from incomplete combustion. Appl. Geochem. 17, 129-162.

Simoneit, B.R.T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H.J., Turpin, B.J., Komazaki, Y., 2004. Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign. J. Geophys. Res., [Atmos] 109, D19S10, doi:10.1029/2004JD004598.

Soja, A.J., Tchebakova, N.M., French, N.H.F., Flannigan, M.D., Shugart, H.H., Stocks, B.J., Sukhinin, A.I., Parfenova, E.I., Chapin, F.S., Stackhouse, P.W., 2007. Climate-induced boreal forest change: Predictions versus current observations. Global and Planetary Change 56, 274-296.

Thevenon, F., Anselmetti, F.S., Bernasconi, S.M., Schwikowski, M., 2009. Mineral dust and elemental black carbon records from an Alpine ice core (Colle Gnifetti glacier) over the last millennium. J Geophys Res-Atmos 114.

Valendik, E.N., 1996. Temporal and spatial distribution of forest fires in Siberia. In J. G. Goldammer and V. V. Furyae (eds), Fire in ecosystems of boreal Eurasia. Kluwer Acadenic Publishers, 129-138.

van der Werf, G.R., Randerson, J.T., Giglio, L., Collatz, G.J., Kasibhatla, P.S., Arellano, A.F., 2006. Interannual variability in global biomass burning emissions from 1997 to 2004. Atmos Chem Phys 6, 3423-3441.

Veltishchev, N.N., Ginsburg, A.S., Colitsyn, G.S., 1988. Climatic effect of mass fires. Izv. Acad. Nauk CCCP Fiz. Atmos. Okeana 27, 296-304 (in Russian with English abstract).

Wong, J., Li, Z.Q., 2002. Retrieval of optical depth for heavy smoke aerosol plume: Uncertainties and sensitivities to the optical properties. J. Atmos. Chem. 59, 250-261.

Table 1. Concentrations of total organic carbon (TOC) and biomass burning tracers in the Ushkovsky ice core with ice chronology.

Core depth (m)	Year A.D.	Concentrations (ng/g-ice)				
		TOC	Levoglucosan	Dehydroabietic acid	Vanillic acid	*p*-Hydroxybenzoic acid
1.1-1.6	1997	1874	0.23	0.111	BDL	BDL
2.2-2.6	1996	1967	0.76	0.238	0.077	0.324
2.6-3.3	1995	1695	0.19	0.096	BDL	0.008
3.3-4.4	1994	1588	0.44	0.248	0.063	0.265
4.8-5.3	1993	1713	0.41	BDL	BDL	0.062
5.3-5.8	1992	1980	0.55	0.248	0.105	0.381
5.8-7.1	1991	1192	0.15	0.111	0.020	0.034
7.1-7.9	1990	1927	0.54	0.056	0.019	0.612
8.4-8.9	1989	1475	1.12	0.037	0.011	0.101
8.9-9.8	1988	1440	0.22	0.050	0.040	0.184
9.8-11.3	1987	1331	0.59	0.038	0.026	0.473
11.3-12.0	1986	2123	0.20	0.108	0.013	0.220
12.3-12.8	1985	1060	0.12	0.069	0.007	0.059
13.0-13.6	1984	1129	0.62	0.107	0.044	0.763
13.6-14.3	1983	1492	0.51	0.067	0.015	0.178
14.3-15.4	1982	757	0.38	0.093	0.022	0.205
15.4-16.5	1981	961	1.52	0.045	0.025	0.599
16.8-17.3	1980	1095	0.36	0.066	BDL	0.171
17.3-17.9	1979	716	0.05	0.059	BDL	0.046
17.9-19.1	1978	730	0.31	0.092	0.030	0.239
19.6-20.1	1977	1102	0.03	0.051	0.021	0.050
20.7-21.5	1976	1236	0.11	0.063	BDL	0.048
21.5-22.6	1975	1836	0.05	0.057	BDL	0.185
22.6-23.5	1974	1213	0.05	0.034	0.009	0.117
23.5-24.1	1973	750	0.11	0.049	0.024	0.117
24.1-24.6	1972	1052	4.82	0.044	0.029	0.578
25.0-25.5	1971	1292	0.73	0.291	0.045	0.279
25.5-25.9	1970	1209	0.36	0.475	BDL	BDL
28.3-28.8	1966	1404	0.71	0.027	0.013	0.170
32.0-32.5	1961	843	0.06	0.016	BDL	0.055
36.3-36.8	1954	979	0.14	BDL	BDL	0.224
39.6-40.1	1949	1783	18.62	0.035	0.071	1.710
44.0-44.5	1942	1071	0.28	0.017	BDL	0.069
48.4-48.9	1933	999	0.44	0.014	BDL	0.223
51.9-52.4	1928	1351	0.61	0.019	BDL	0.127
56.1-56.6	1922	1124	0.16	0.008	BDL	0.021
60.1-60.5	1915	1068	1.81	0.007	BDL	0.325
64.9-64.4	1908	769	0.05	BDL	BDL	0.037
67.9-68.4	1897	639	0.05	BDL	BDL	0.050
72.1-72.6	1889	750	0.25	0.006	BDL	0.139
76.4-76.9	1883	876	2.20	0.007	BDL	0.032
81.0-81.5	1871	673	0.04	0.007	BDL	ND
84.9-85.4	1862	883	0.02	BDL	BDL	0.026
88.8-89.3	1854	722	BDL	0.006	BDL	BDL
92.4-92.9	1847	1178	0.12	BDL	BDL	BDL
95.9-96.4	1840	692	0.02	0.004	BDL	BDL
99.9-100.4	1832	857	0.05	BDL	BDL	BDL
104.2-104.7	1818	960	0.04	BDL	BDL	BDL
108.1-108.6	1809	804	0.01	BDL	BDL	BDL
111.6-112.1	1800	753	0.08	BDL	BDL	0.130
115.7-116.2	1790	761	0.78	BDL	BDL	0.044
120.8-121.3	1778	915	0.06	BDL	BDL	0.210
124.7-125.1	1768	1364	0.40	0.012	BDL	0.270
128.1-128.6	1759	1285	4.81	0.010	0.127	1.741
132.3-132.8	1748	959	0.59	0.004	BDL	0.042
136.9-137.4	1736	1127	0.18	BDL	BDL	0.295
140.0-140.6	1727	1109	0.43	0.005	BDL	0.307
144.6-145.1	1715	1729	0.08	0.025	BDL	0.113
148.0-148.6	1705	1302	1.59	0.026	0.064	1.439
152.1-152.6	1693	1167	BDL	BDL	BDL	BDL
155.8-156.3		1163	0.10	BDL	BDL	0.017
159.7-160.2		1281	0.44	0.010	BDL	0.013
163.5-164.0		2604	0.34	0.029	BDL	0.087
168.9-169.5		1191	0.11	BDL	BDL	0.020
171.3-171.8		2241	0.02	BDL	BDL	0.095
176.8-177.3		758	1.11	0.019	BDL	0.074
180.2-180.7		1075	2.34	0.026	0.030	0.430
184.7-185.3		406	0.12	0.006	BDL	BDL
188.3-188.7		1714	0.06	0.015	BDL	0.027
191.0-191.5		871	0.05	0.006	BDL	0.232

196.4-196.9	1004	0.29	0.012	0.009	0.038
199.6-200.0	1507	0.95	0.009	BDL	0.016
203.2-203.7	854	0.14	0.009	BDL	0.034
208.2-208.7	1048	0.25	0.011	BDL	0.037
209.4-209.9	1170	0.10	0.025	BDL	0.029

BDL: Below detection limit, Detection limits: 0.003 to 0.005 ng/g-ice depending on the species (for more detail, see the text).

Figure captions

Fig. 1. Map of the Kamchatka Peninsula with the sampling site of the Ushkovsky ice core at the ice cap of Ushkovsky volcano.

Fig. 2. Historical change in the concentrations of total organic carbon (TOC) in the Ushkovsky ice core taken from the Kamchatka Peninsula.

Fig. 3. (a) Typical GC/MS trace (total ion current: TIC) of trimethylsilylated total extracts isolated from the Ushkovsky ice core sample (FA: fatty acids, A: alkanes, ●: unknown monosaccharide), (b) mass spectra of levoglucosan-TMS, (c) mass spectra of vanillic acid-TMS and (d) mass spectra of *p*-hydroxybenzoic acid-TMS.

Fig. 4. Historical variations of (a) levoglucosan, (b) dehydroabietic acid, (c) vanillic acid, and (d) *p*-hydroxybenzoic acid in the Ushkovsky ice core.

Fig. 5. Seven days backward trajectory analyses at Ushkovsky for 4 seasons (a) MAM; March, April and May, (b) JJA; June, July and August, (c) SON; September, October and November, and (d) DFJ; December, January and February, throughout 2001. The trajectory calculations were performed everyday from the Ushkovsky site (56.07°N and 160.47°E) at 4500 m above sea level. Each color trajectory line indicates tracing time from sampling point, red: 0-3 days, yellow: 3-5 days and blue: 5-7 days.

Fig. 6. Estimated annual emission of total particulate matter (TPM) from fires in the Northern Hemisphere for 2001. Original data are in Global Fire Emission Database version 2.1 (GFEDv2.1) (http://daac.ornl.gov/VEGETATION/guides/global_fire_emissions_v2.1.html). Monthly TPM data are summed for 2001.

Fig. 1

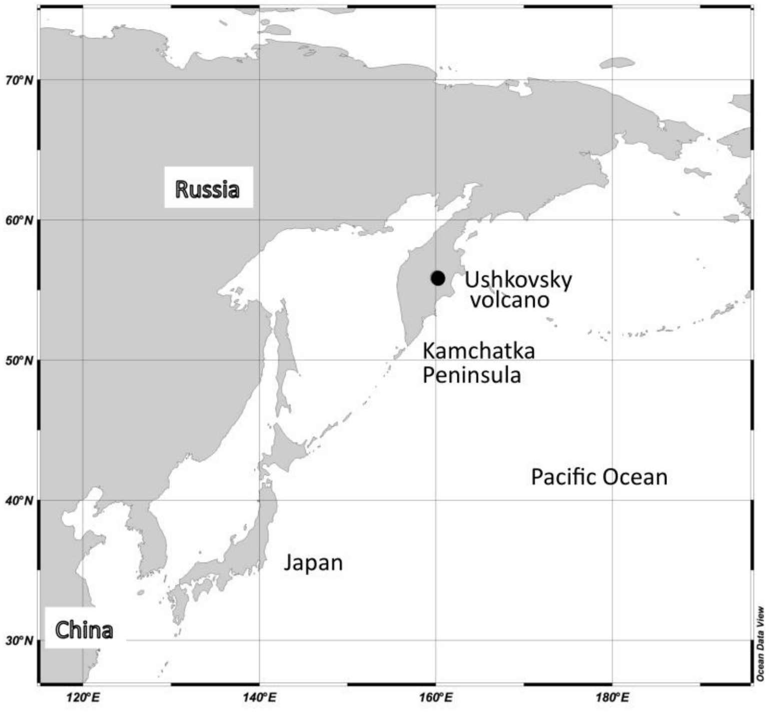

Russia
Ushkovsky volcano
Kamchatka Peninsula
Pacific Ocean
Japan
China
70°N
60°N
50°N
40°N
30°N
120°E
140°E
160°E
180°E
Ocean Data View

Fig. 2

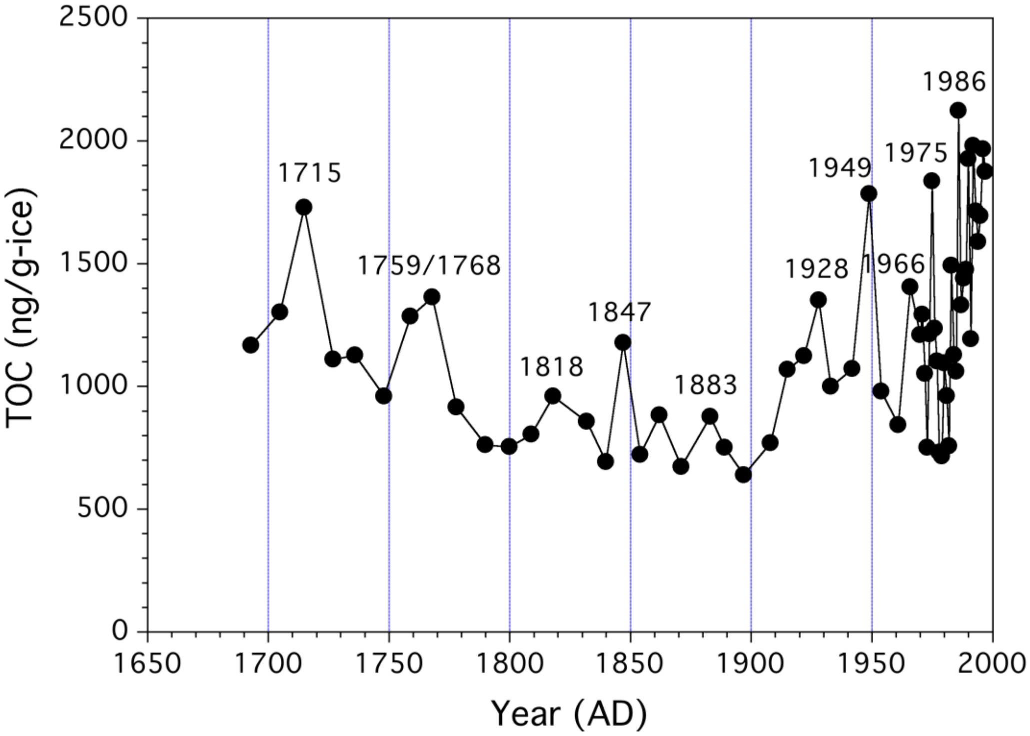

TOC (ng/g-ice)
Year (AD)
0
500
1000
1500
2000
2500
1650
1700
1750
1800
1850
1900
1950
2000
1715
1759/1768
1818
1847
1883
1928
1949
1966
1975
1986

Fig. 3

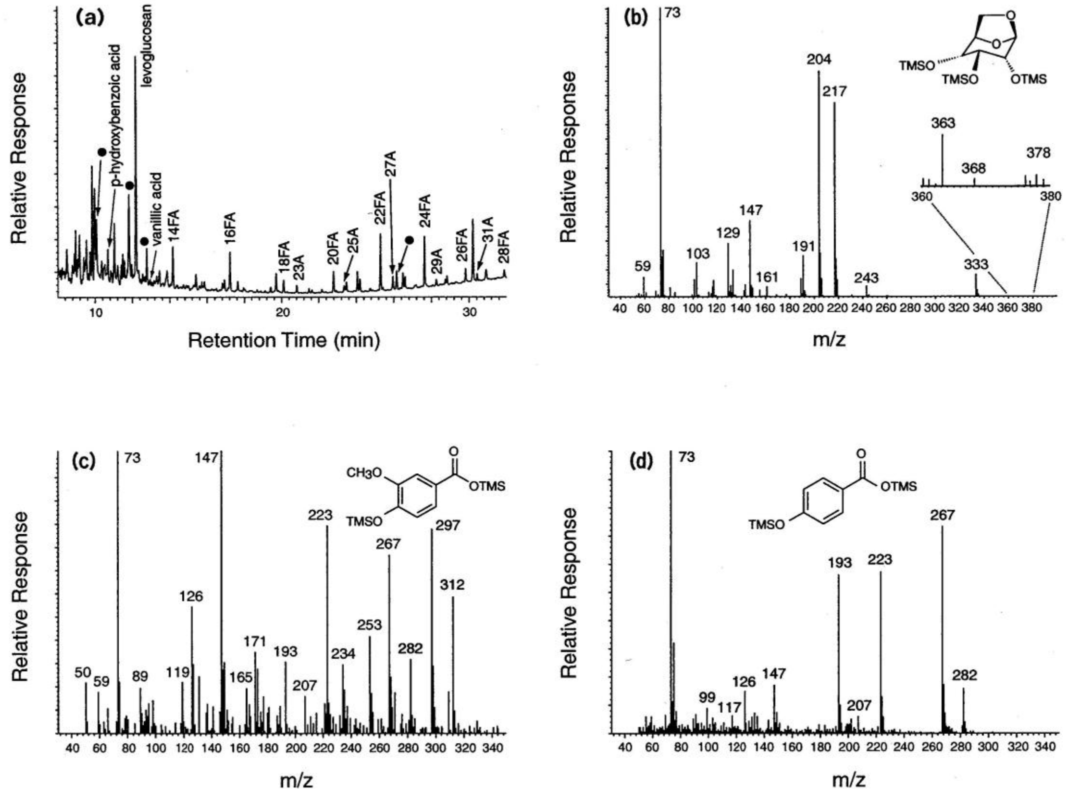

(a)
Relative Response
Retention Time (min)
p-hydroxybenzoic acid
levoglucosan
vanillic acid
14FA
16FA
18FA
23A
20FA
25A
22FA
27A
24FA
29A
26FA
31A
28FA
10
20
30
(b)
73
59
103
129
147
161
191
204
217
243
333
363
368
378
360
380
TMSO
TMSO
OTMS
m/z
(c)
73
147
50
59
89
119
126
165
171
193
207
223
234
253
267
282
297
312
CH3O
TMSO
OTMS
m/z
(d)
73
99
117
126
147
193
207
223
267
282
TMSO
OTMS
m/z

Fig. 4a

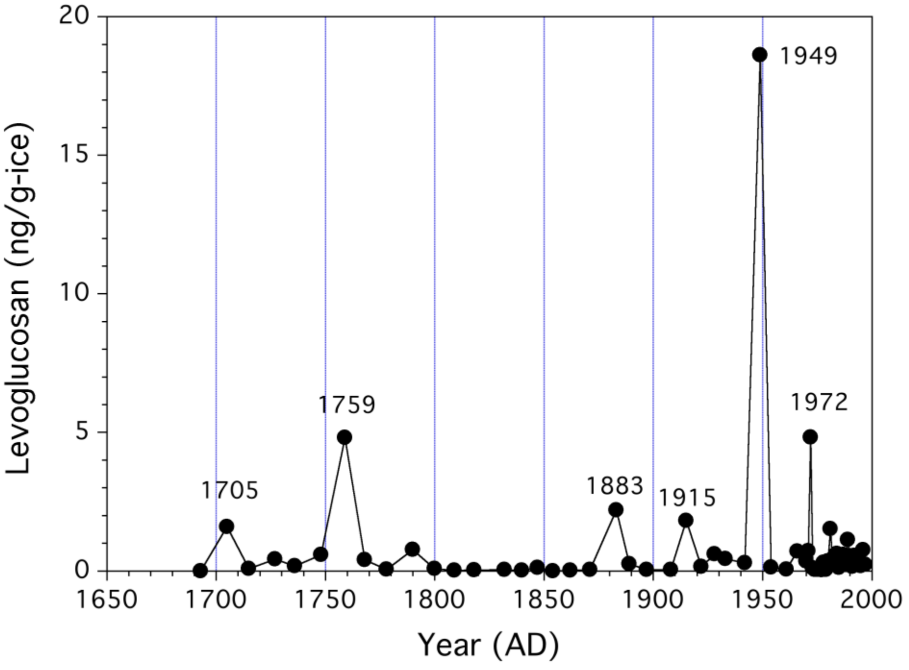

Levoglucosan (ng/g-ice)
Year (AD)
0
5
10
15
20
1650
1700
1750
1800
1850
1900
1950
2000
1705
1759
1883
1915
1949
1972

Fig. 4b

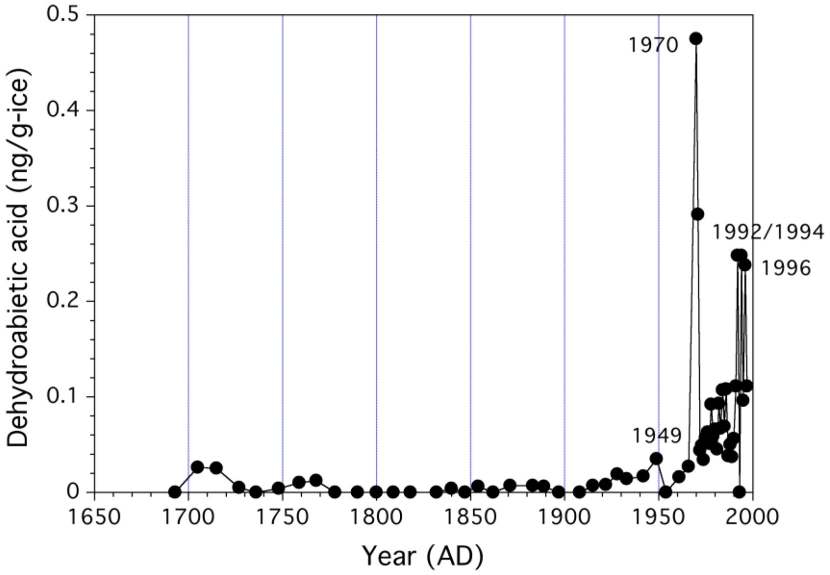


Fig. 4c

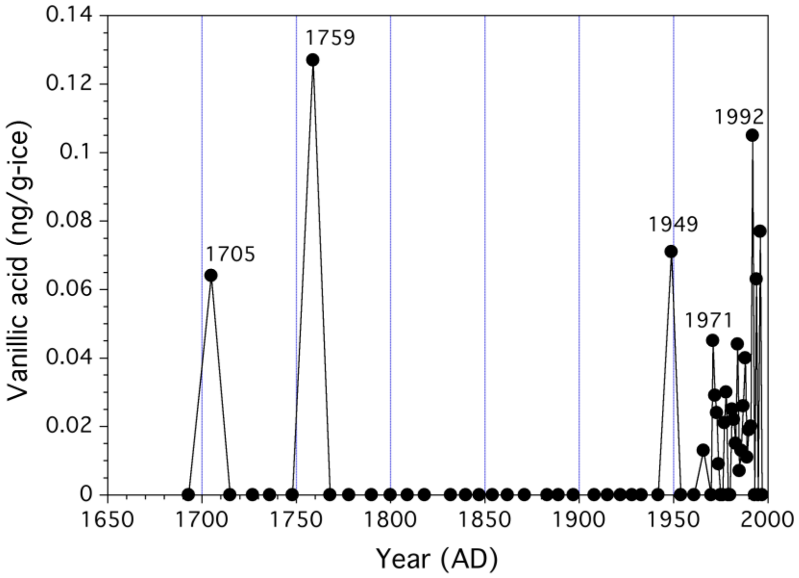


Fig. 4d

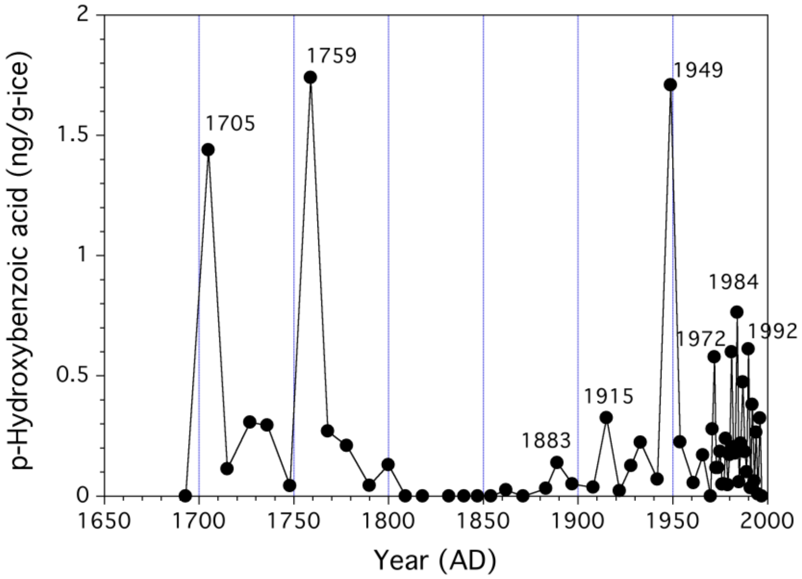


Fig. 5

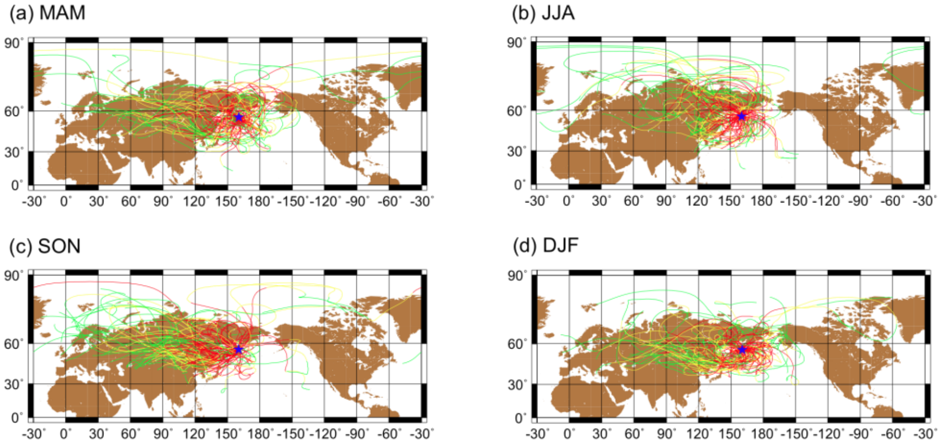
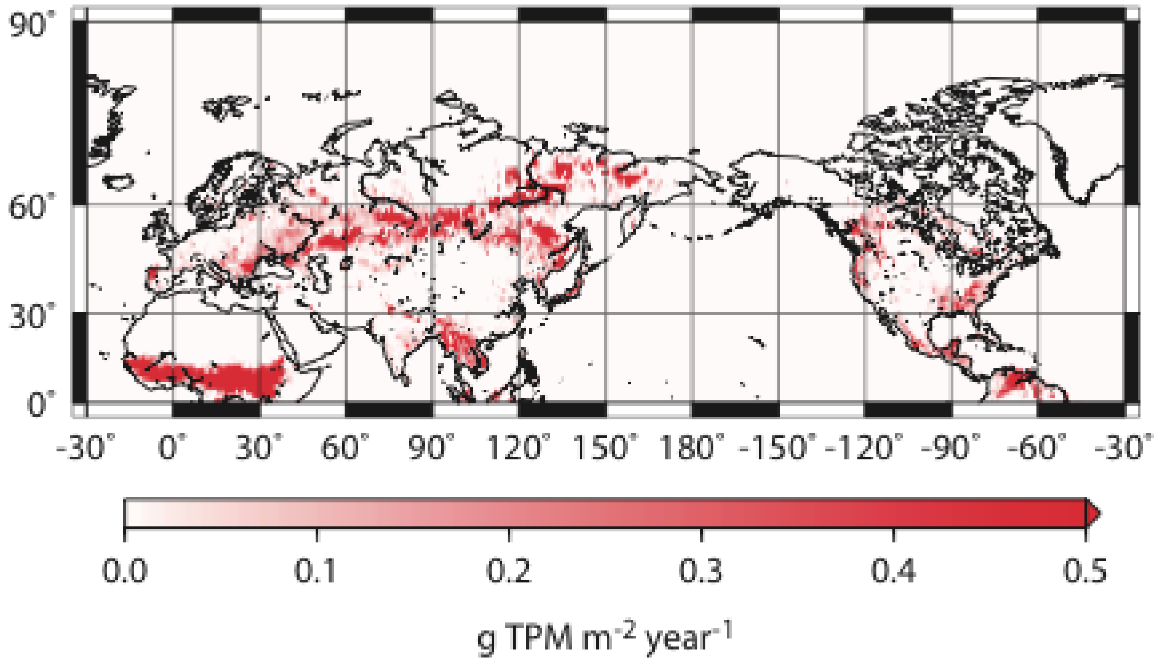

(a) MAM
(b) JJA
(c) SON
(d) DJF
90˚
60˚
30˚
0˚
-30˚ 0˚ 30˚ 60˚ 90˚ 120˚ 150˚ 180˚ -150˚ -120˚ -90˚ -60˚ -30˚

Fig. 6


90°
60°
30°
0°
-30°
0°
30°
60°
90°
120°
150°
180°
-150°
-120°
-90°
-60°
-30°
0.0
0.1
0.2
0.3
0.4
0.5
g TPM m^{-2} year^{-1}