The referee raised several good points and we appreciate the comments. The manuscript has been modified as described below to take them into account. Referee comments are in normal font and our responses are in bold.

1. I saw that you have evaluated the charcoal records on the supplementary information, but I think that this part should be reported in the main manuscript with other considerations.

   As recommended, the comparison to charcoal records has been moved into the Results and Discussion section of the main manuscript as Section 3.5.

2. I suggest to insert a new paragraph in the main manuscript with the comparison with other biomass burning proxy records. For example, Rubino et al (2015) reported that ammonium and nss -K can be used as biomass burning proxies, and these data are available in the same ice core (Wendl, ACP, 2015). Some authors of this paper have collaborated to publish the paper of aromatic acids in the Akademii Nauk ice core, in which a good comparison with other proxies (for example with levoglucosan) is reported. Introduction. Page 2. Lines 1-10. You reported only a list of possible biomass burning tracers, but I suggested to better describe the advantages and the disadvantages of each marker. I recommend to improve this part of the introduction.

   The text in the introduction has been expanded as suggested.

3. In the manuscript (and also in the title), the authors consider p-hydroxybenzoic acid as a methoxy aromatic acid but p-HBA does not have the methoxy moiety. Please check and correct. Specific comments Title. The use of "methoxy" in the title is wrong because phydroxybenzoic acid is not a methoxy phenol. I suggest to remove "methoxy".

   We greatly appreciate the reviewer catching this obvious (and embarrassing) mistake! "Methoxy" is now removed from the title and the rest of the manuscript.

4. Page 4. Line 32. You detected VA using two different transitions (167>108 and 167>152) while p-HBA with only one transition (137>93). The quantitative method using HPLC-MS/MS or IC-MS/MS requires the monitoring of two transitions where the most intense transition was used to quantify the compound and the other one was used to confirm the identity of compound.

   Unfortunately, p-HBA has only one mass transition representing a significant fraction of the total signal (137→93). It was therefore not possible to confirm identity using another mass transition. We have seen no evidence in terms of peak shape or retention time to cast doubt on the identity of the peak.

5. Page. 5. Line 5. Have you evaluated the contamination during the proceeding? Have you subtract the blank values?

   For this study, full procedural blanks covering field collection and sample melting were not available. We did routinely analyze laboratory blanks along with samples.

These did not exhibit detectable peaks at the mass transitions for VA or p-HBA. During this and previous studies, we have not experienced contamination of these compounds at significant levels.

As noted in the Methods section, the limits of detection were calculated using 3x the standard deviations of the blank. Measurements at or below the detection limit were reported as ½ of the limits of detection.

6. Page 5. Line 8. You reported that you analyzed 993 samples, but in page 4-line 26 you wrote that you had 997 samples. Please correct this discrepancy.

   We collected 997 samples but analyzed only 993. The text has been modified to refer only to the number analyzed.

7. Page 7. Lines 25-31 and figure 7. Why you have reported two different NAO indexes from two different references? Which is the difference between two records?

   We agree that the two NAO records were similar and removed the shorter of the two records.

8. Page 10. Paragraph 3.6. In this paragraph you described the behavior of proxies and their possible modification occurred due to atmosphere/snow interactions. I think that the discussion about "potential for post depositional modification of VA and p- HBA" should be reported before of "Relationship to atmospheric circulation and climate".

   Agreed. The discussion of postdepositional modification is now Section 3.3.

9. Abstract. Line 5. Please correct "1,000 ng/l" with "1,000 ng L-1)

   Done

10. Page 5. Line 10. Please add "limit" after "detection".

    "Below detection" was changed to "below the limits of detection."

11. Page 5. Line 10. Please add "0" before of ".006".

    Done

12. Figures 6 and 8. Please can you specify the period that you consider to calculate the back trajectories.

    These figures are now figures 7 and 9. The figure 7 caption was revised as follows: Figure 7. "…10-day back trajectories from 2006-2015 reaching the boreal ecosystems starting from the Lomonosovfonna and Akademii Nauk ice core locations…."

Figure 9 has been removed and replaced with a different figure.

The referee raised several points and we appreciate the comments. The manuscript has been modified as described below to take the comments into account. Referee comments are in normal font and our responses are in bold.

1. Checking the ammonium profile (Figures 3 and 4 in Wendl et al.), I see three time periods with elevated ammonium levels (around 1370, 1545, and 1900) but nothing in 1300. Can we conclude from that ammonium is not an adequate biomass burning tracer in this region? Is this difference for ammonium between Arctic and Greenland sites related to difference of altitude of plumes (more scavenging at the low elevated marine site of Svalbard???).

   In an effort to answer this question, we attempted a quantitative examination of the co-variability of Lomonosovfonna VA, p-HBA, and ammonium. The results are reported in section 3.4.

2. Abstract: Please specify for which season air mass back trajectories were computed and for how many days.

   Page 1, line 9 was changed to "10-day air mass back trajectories for a decade of fire seasons (March-November, 2006-2015) indicate that Siberia and Europe are the principle modern source regions for wildfire emissions reaching the Lomonosovfonna site."

3. Page 4, Line 5-8: Please specify for how many days air mass back trajectories were computed.

   Page 4, Lines 5-8 were changed to: "The 10-day back trajectories were started at 100 m above the ice surface at 12:00 AM and 12:00 PM local time for three separate 10-year periods, 1948-1957, 1970-1979, and 2006-2015 CE."

4. Page 2, line 9: Please clarify the reference Rubino et al. (2015): In my record the paper had appeared in 2016:

   Corrected.

5. Page 6, Line 30-33: Please specify for how many days air mass back trajectories were computed for both sites (5 days ?, 10 days ?).

   Page 6, Lines 30-33 were changed to "10-day back trajectories were computed for the Akademii Nauk site using the same methods as those described above from 2006-2015 CE (section 2.2; Grieman et al., 2017). The 10-day back trajectories show that both Lomonosovfonna and Akademii Nauk sites are influenced by air masses transecting Eurasian forested regions (Fig. 7; Table S1).

6. Figure 7: Sodium at GISP 2: This figure will not really convince the reader that the NAO influences the sodium record in central Greenland.

These data did not add much to the discussion and have been removed from figure 8.

7. By the way, what tell us the sodium record at the Svalbard site (available in Wendl et al., 2015) in Figure 3 and 4.

The sodium record for this core published by Wendl shows a long term declining trend, with centennial variability that is generally similar in character to VA, p-HBA and other parameters in this core. The Wendl et al. (2015) paper provided little discussion about the causes of the sodium variability. Presumably, the seasalt record reflects changes in the frequency of air mass trajectories from the North Atlantic, as well as the intensity of storms and one might speculate that both could be related to changes in the phase of the NAO. A serious analysis of seasalt data covering the period of satellite era would be worthwhile, but outside the scope of this paper.

The referee raised several points and the comments are appreciated. The manuscript has been changed as described below to take them into account. Referee comments are in normal font and our responses are in bold.

Page 1 Lines 5 and 6: "Vanillic acid levels are high (below the limit of detection to 0.1 ppb) from 1200-1400 CE, then gradually decline into the 20th century." Concentrations below the level of detection cannot be high by definition.

This sentence has been changed to: "Vanillic acid levels are high (maximum of 0.1 ppb) from 1200-1400 CE, then gradually decline into the 20th century."

Page 1 Line 9 to 10: Are Siberia and Europe the primary source regions throughout the time period of the entire study? Or are they the primary modern source regions?

This sentence has been changed to: "10-day air mass back trajectories for a decade of fire seasons (March-November, 2006-2015) indicate that Siberia and Europe are the principle modern source regions for wildfire emissions reaching the Lomonosovfonna site."

Lines 19 to 20: "Boreal wildfire areal extent appears to have increase significantly with warming during the past few decades" needs a citation.

This sentence has been removed.

Page 3 Lines 20-29: Why do you use ten-year bin averages rather than, for example, 10-year moving averages? If the dating uncertainty below 80 m is 10 years, then are ten-year bin averages too narrow of a time frame? It is essential to explain your reasoning in this section.

The choice of bin-averaging over moving averages is not significant. To demonstrate this, we added moving averages to Figure S8 for comparison to the bin average. The differences between the two are very slight and would not impact the interpretation.

We note that the dating uncertainty is an issue of absolute age assignment, not time resolution, so it is not really related to the issue of resolving signals.

Page 4 Line 5: Why did you choose to start the trajectories at 100 m above the ice surface?

We were initially concerned about how representative ground-level back trajectories would be given the potential for shallow, highly stable boundary layers, inversions, etc. So, we conducted trajectories starting at multiple levels from the surface to 500m above surface. These all gave very similar results. We arbitrarily selected 100m.

Page 4 Lines 8 and 9: What is the latitudinal boundary for North America, Siberia and Europe in your study?

The following sentence was added beginning on Page 4, lines 19-20: "The boundaries of North America, Siberia and Europe were defined using global self-consistent, hierarchical, high-resolution geography database GIS shapefiles (Wessel et al., 1996)."

Wessel, P., and W. H. F. Smith, A Global Self-consistent, Hierarchical, High-resolution Shoreline Database, *J. Geophys. Res., 101*, 8741-8743, 1996

Section 3.1: Either refer to this section in Page 3 Lines 20-29 or else move the entire section to immediately follow the current Page 3 lines 20-29 where you first describe that you use 10-year bins for your data.

A reference to Section 3.1 has been added to Page 4, line 10: "Ten-year bin averages are used to illustrate short-term variability in the data (see Section 3.1)."

Page 5 Lines 13 and 14: Were the geometric means and standard deviations used because of the skewness? I think that this is what you would like to say, but please rephrase to your meaning is clear.

Page 5, Lines 26-28 were changed to the following: "Geometric means and standard deviations were used for all statistics because the frequency distribution of the data was skewed towards lower concentrations."

Page 5 Line 15: At the deepest section of the core, how many samples do you have in each 10-year bin?

The time bin from 1221-1225 contains two samples. The first 10-year time bin from 1225-1235 contains 4 samples. The long-term declining trend also is shown using 40-year bin averages.

Page 5 Lines 28-30: Can this long-term decreasing trend be caused by decomposition or degradation of VA and p-HBA through time? (Refer the reader to Section 3.6 to demonstrate that you have considered these possibilities).

Degradation of VA and p-HBA would cause a long-term increasing trend because VA and p-HBA deeper in the ice core would have degraded.

Section 3.4 and Conclusions: Stating that an "atmospheric reorganization" due to changes in the SNAO affects the differences in biomass burning tracers is quite a bold statement. Although you describe the spatial patterns of the SAO, a figure can better demonstrate the influence of the SNAO on transport affecting these two ice cores sites. The back trajectories for the positive SNAO index (1970-1979 CE) and negative (1948-1957 CE) can help depict the source regions and transport paths. Figure 2 of Folland et a., (2009) is an excellent example of the spatial extent of the summer NAO. However, plotting an example of the spatial patterns for a positive SNAO (1970-1979 CE) and negative SNAO index (1948-1957 CE) can also add essential support to your argument.

We agree that the statement was perhaps too strong. We revised Page 10, line 15 to: "We suggest that a change of high latitude northern hemisphere atmospheric circulation patterns occurred at this time,…".

We took the suggestion to make a new figure. Figure 9 was removed because it did not add to the argument. Figure 9 was replaced with a new figure. The following text has been

added, Page 10, lines 32-35: "Figure 9 shows the major spatial clusters of 10-day air mass back trajectories for each time period (computed using Hysplit) superimposed on the sea level pressure (SLP) anomalies relative to mean SLP from 1948-2017. The high SNAO period is characterized by 1) high pressure over Scandinavia, favoring drier conditions, and 2) trajectories generally originating at lower latitudes, with a larger fraction of transport from Scandinavia."

Section 3.5: You mention that "the long-term trends in the VA/p-HBA ratio presumably reflect changes in the relative contributions of fuel types or changes in atmospheric transport". I kept expecting you to tie these possible changes in atmospheric transport back to the discussion of the SNAO. This lack of a mention of causes of these atmospheric changes is surprising in light of the previous section.

The following has been added to section 3.8, page 11, lines 31-34 and page 12, lines 1-2: "There are significant long-term changes in the Lomonosovfonna VA/p-HBA ratio over time. The ratio is relatively high during the MCA (0.8), decreases by a factor of two from 1200-1400 CE, remains low through the LIA until around 1800 CE (Fig. 3). There is also an increase in VA/p-HBA after 1800, although VA is close to the detection limit and the uncertainty in the ratio is consequently large. Interestingly, the changes in the VA/p-HBA ratio broadly mirror changes in the phase of the paleoreconstructions of the NAO and SNAO (Fig. 8). One might speculate that the associated changes in climate and transport mentioned earlier contribute to the variations in the VA/p-HBA ratio but the specific causes are not understood at this time."

Relevant Changes made to the Manuscript

1. “Methoxy” has been removed from the title.
2. The introduction has been expanded to include more tracers.
3. Section 3.3: Potential for post depositional modification of VA and p-HBA has been moved up from section 3.6
4. Section 3.4 Relationship to ammonium record was added.
5. Section 3.5: Relationship to sedimentary charcoal records has been added.
6. Section 3.8: Lomonosovfonna ice core VA/p-HBA ratios has been revised.
7. The shorter NAO record was removed from figure 8.
8. The GISP2 sodium record was removed from figure 8.
9. Figure 9 was replaced with a new back trajectory figure.

~~Methoxy aromatic~~ Aromatic acids in an Arctic ice core from Svalbard: a proxy record of biomass burning

Mackenzie M. Grieman[1], Murat Aydin[1], Elisabeth Isaksson[2], Margit Schwikowski[3], and Eric S. Saltzman[1]

[1]Department of Earth System Science, University of California, Irvine, Irvine, California, 92697-3100, USA
[2]Norwegian Polar Institute Fram Centre NO-9296, Tromsø, Norway
[3]Paul Scherrer Institute, Villigen, Switzerland and Oeschger Centre for Climate Change Research, University of Bern, Switzerland

Correspondence to: Mackenzie M. Grieman (mgrieman@uci.edu)

Abstract. This study presents vanillic acid and para-hydroxybenzoic acid levels in an Arctic ice core from Lomonosovfonna, Svalbard covering the past 800 years. These ~~methoxy~~ aromatic acids are likely derived from lignin combustion in wildfires and long-range aerosol transport. Vanillic and para-hydroxybenzoic acid are present throughout the ice core, confirming that these compounds are preserved on millennial time scales. Vanillic and para-hydroxybenzoic acid concentrations in the Lomonosovfonna ice core ranged from below the limits of detection to 0.2 and 0.07 ppb, respectively (1 ppb = 1,000 ng ~~/~~L^{-1}). Vanillic acid levels are high (~~below the limit of detection to~~ maximum of 0.1 ppb) from 1200-1400 CE, then gradually decline into the 20th century. The largest peak in the vanillic acid in the record occurs from 2000-2008 CE. In the para-hydrobenzoic acid record, there are three centennial-scale peaks around 1300, 1550, and 1650 CE superimposed on a long-term decline in the baseline levels throughout the record. ~~Air mass back trajectory analysis indicates~~ 10-day air mass back trajectories for a decade of fire seasons (March-November, 2006-2015) indicate that Siberia and Europe are the ~~primary~~ principle modern source regions for wildfire emissions reaching the Lomonosovfonna site. The Lomonosovfonna data are similar to those from the Eurasian Arctic Akademii Nauk ice core during the early part of the record (1220-1400 CE), but the two ice cores diverge markedly after 1400 CE. This coincides with a shift in North Atlantic climate marked by a change of the North Atlantic Oscillation from a positive to a more negative state.

1 Introduction

Biomass burning influences the biosphere, atmospheric chemistry, and the climate system on both regional and global scales. Fire influences ecosystem dynamics, ecohydrology, surface albedo, and emissions of chemically and radiatively active aerosols and gases (Crutzen and Andreae, 1990; Legrand et al., 2016; Hessl, 2011; Bowman et al., 2009; Randerson et al., 2006). In boreal regions, fire plays a stabilizing role in circumboreal successional dynamics, influencing ~~boreal~~ forest age structure, species composition, and floristic diversity (Soja et al., 2007). Boreal ~~wildfire areal extent appears to have increased significantly with warming during the past few decades. Boreal~~ forest burned area, fire frequency, fire season length, and fire severity will likely

increase with continued warming (Soja et al., 2007; Chapin et al., 2000). Arctic tundra fires are of particular concern because of their potential to release large amounts of ancient permafrost carbon into the atmosphere (Mack et al., 2011).

Understanding the role of fire in the climate system requires a knowledge of past regional/temporal variations ~~and their relationship to climate change~~ on decadal, centennial, and millennial time scales. A number of ~~different types of~~ proxy fire records have been developed from sediment cores and ice cores but systematic reconstruction of fire history remains a major challenge. ~~Global and regional reconstructions of biomass~~ Terrestrial sedimentary charcoal records are inherently local in extent, but regional and even global trends in burning have been developed ~~using sedimentary charcoal records~~ from these records using various normalizing and averaging methods (Marlon et al., 2008, 2016; Power et al., 2008, 2013). The ~~charcoal database~~ global charcoal database (GCD: Blarquez et al., 2014) is spatially and temporally inhomogeneous across the northern hemisphere boreal and Arctic regions, with good coverage in regions of North America and Western Europe, and poor coverage in Asia~~(accessed at: http://gpwg.paleofire.org; Blarquez et al., 2014). Chemical analyses of inorganic, organic, ~~. Dissolved and particulate constituents in ice ~~core melt water~~ cores have also been used ~~to reconstruct past variability in biomass burning~~ as burning proxies. These include ~~burning derived markers such as ammonium , organic acids, potassium, and black carbon (see Legrand et al., 2016; ?, for recent reviews)~~cations (ammonium, potassium), anions (formate, acetate, nitrate), and black carbon (see Legrand et al., 2016; Rubino et al., 2016, for recent reviews). One of the challenges of interpreting these records is that most of the dissolved ions have multiple sources, in addition to burning. For example, ammonium is also derived from biogenic marine and terrestrial sources, agriculture, and livestock (Legrand et al., 1992, 2016; Fuhrer et al., 1996; Savarino and Legrand, 19 Efforts to isolate the fire-derived contributions to these records have employed principle component analysis and peak counting methods. Eichler et al. (2009) examined a Siberian Altai ice core using a multiproxy approach, and concluded that potassium, nitrate, and charcoal were fire-related while ammonium and formate were biogenic in origin. The detailed interpretation of ice core chemical proxies is complicated by the fact that black carbon is emitted primarily during the flaming conditions, while ammonium and many organic aerosol-borne constitutents are emitted primarily during smoldering. Ice core gas measurements of methane and carbon monoxide, and their isotopomers, have also been used to derive histories of pyrogenic emissions (Ferretti et al., 2005; Wang et al., 2010). These gases have sufficiently long atmospheric lifetimes that they integrate emissions over hemisphere/global scales.

~~Methoxy aromatic~~ A variety of organic aerosols are emitted from the burning of vegetation under smoldering conditions. Levoglucosan, a combustion product of cellulose, is considered a universal biomass burning tracer because it is emitted in greater quantities than most other burning-derived organic aerosols and is uniquely produced by the burning of plant matter (Simoneit et al., 1999). Levoglucosan has been detected in ice cores from Antarctica, Greenland, and northeast Asia (Gambaro et al., 2008; Kawamura et al., 2012; Zennaro et al., 2014). It is considered a qualitative tracer because it degrades rapidly in the atmosphere (Hoffmann et al., 2010; Hennigan et al., 2010; Legrand et al., 2016; Slade and Knopf, 2013).

Aromatic acids are among a wide range of phenolic compounds generated by lignin pyrolysis. These compounds are ubiquitous constituents of biomass burning aerosols and have been detected in polar ice cores. Lignin is produced from three precursor alcohols (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol), and the resulting phenolic compounds retain the structure of these alcohols. The aromatic acids analyzed in this study are vanillic acid (VA) and p-hydroxybenzoic acid

(p-HBA). VA is predominantly associated with conifer and deciduous boreal forest tree species, while tundra grasses and peat generate primarily p-HBA with lesser amounts of VA (Simoneit, 2002; Oros and Simoneit, 2001a, b; Oros et al., 2006; Iinuma et al., 2007). p-HBA is also produced from conifer boreal tree species (Oros and Simoneit, 2001a).

Burning is the only known source of these ~~methoxy~~ aromatic acids in aerosols or ice cores. Quantitatively, the ice core levels of these compounds result from the combined effects of emissions, atmospheric transport, depositional, and perhaps post-depositional processes. Aromatic acids can undergo re-volatilization at the snow surface. Laboratory experiments have shown that Arctic snow samples containing lignin-derived compounds photochemically react to produce formaldehyde and acetaldehyde (Grannas et al., 2004). Melting and refreezing processes have the potential to redistribute aromatic acids to lower depths. Meltwater at the surface percolates to deeper snow layers and water-soluble compounds are concentrated when the meltwater is refrozen (Wendl et al., 2015).

Prior studies of pyrogenic aromatic acids in ice cores include shallow cores from Greenland, northeast Asia (Kamchatkan Peninsula), and Europe (the Swiss Alps) (McConnell et al., 2007; Kawamura et al., 2012; Müller-Tautges et al., 2016). The record from Greenland showed that the timing of variability in the VA and black carbon records was similar over the past 200 years until around 1890 CE (McConnell et al., 2007). VA and p-HBA were elevated from the 1950's to the 1970's in the 60-year ice core record from the Swiss Alps (Müller-Tautges et al., 2016). VA and p-HBA were elevated in the 1700's and in the 20th century in the ice core from Northeast Asia over the past 300 years. There is only one millennial time scale ice core record of VA and p-HBA: a 2600-year Akademii Nauk ice core record from the Eurasian Arctic (Grieman et al., 2017). That record showed three major multi-century pulses of burning-derived aromatic acids, including one during the Little Ice Age (1450-1700 CE).

Here we present measurements of vanillic acid (VA) and p-hydroxybenzoic acid (p-HBA) in an Arctic ice core from the Lomonosovfonna ice cap in central Spitsbergen, Svalbard, which is located northeast of Greenland, in the Atlantic sector of the Arctic ocean (Fig. 1). The goal of this study was to generate a record sensitive to conditions in Northern Europe/Northern Eurasia. Air mass back trajectories are used to examine the distribution and ecology of likely source regions for biomass burning aerosols transported to Svalbard. We discuss the variability observed in the ice core records of these compounds over the past 750 years, and compare the records to other proxy records of northern hemisphere climate and biomass burning.

2 Methods

2.1 Ice core site characteristics and dating

The Lomonosovfonna ice core site is 1202 m above sea level (asl) (78.82°N, 17.43°E) (Fig. 1). The ice core was drilled in 2009 to a depth of 149.5 m by a team from the Paul Scherrer Institute and the Norwegian Polar Institute. The core did not reach bedrock and contains a continuous 750-year record ~~with a basal ice age of 1222 CE~~ (Wendl et al., 2015). The near-surface annual average temperature of Lomonosovfonna is -12.5°C at 1020 m asl (Beaudon et al., 2013; Pohjola et al., 2002; Zagorodnow, 1988). The annual average accumulation rate is 0.58 $\pm$ 0.13 m water equivalent (meq) year^{-1} (Wendl et al., 2015). The firn/ice transition occurs at 13 m depth, at approximately 1997 C.E.

The Lomonosovfonna ice core was dated by Wendl et al. (2015), yielding a time span for the core of 1222-2009 CE (Fig. S1). Annual layers were counted using seasonal $\delta^{18}O$ and Na^+ variations to a depth of 97.7 m (79.7 m weq), giving an age of 1750 CE at that depth. The chronology of the upper section of the core was also constrained by the ^{210}Pb profile and the 1963 ^3H horizon. The age scale below 97.7 m was developed using a simple glacier ice flow model (Thompson et al., 1998), assuming an average accumulation rate of 0.58 $\pm$ 0.13 m weq year^{-1} (Wendl et al., 2015). The age scale was adjusted to match seven volcanic reference horizons. The oldest of these is the Samalas volcanic eruption of 1257/8. Dating uncertainty was estimated by comparing purely modelled reference horizon years to known volcanic eruption years. Above 68 m weq, the dating uncertainty is $\pm$1 year within 10 years of reference horizons, and $\pm$3 years otherwise. Between 68-80 m weq, the dating uncertainty is $\pm$3 years, and below 80 m weq, the dating uncertainty is $\pm$10 years (Wendl et al., 2015).

The Lomonosovfonna site experiences summer surface melting and winter refreezing (Wendl et al., 2015). Wendl et al. (2015) examined the distribution of melt layers in the Lomonosovfonna ice core, concluding that most summer melt layers are refrozen within the year, with some extending over 2-3 years. The frequency of melt layers increases after 1800 CE (Fig. S2; Wendl et al., 2015). During the warmest years of the twentieth century, percolation length reached 8 years. Due to possible redistribution of soluble compounds by melt, percolation, and refreezing, inter-annual variability of the aromatic acid signals is not interpreted in this study. Ten-year bin averages are used to ~~discuss~~ illustrate short-term variability in the data (see Section 3.1).

2.2 Potential source regions and ecological types using air mass back trajectories

Air mass back trajectories were used to identify potential source regions and ecofloristic zones from which biomass burning aerosols are likely to reach the Lomonosovfonna ice core site. This analysis assumes modern-day meteorological conditions. 10-day air mass back trajectories were computed using the HYSPLIT model with NCEP/NCAR Reanalysis data (Draxler et al., 1999; Stein et al., 2015; Kalnay et al., 1996). The 10-day back trajectories were started at 100 m above the ice surface at 12:00 AM and 12:00 PM local time for three separate 10-year periods, 1948-1957, 1970-1979, and 2006-2015 CE. The fraction of trajectories originating in or transecting various geographic regions and ecofloristic zones was calculated for spring (March 1-May 31), summer (June 1-Aug. 31), and fall (Sept. 1-Nov. 30). The geographic regions included in the study were North America, Siberia (>42°E), and Europe (<42°E). The boundaries of North America, Siberia, and Europe were defined using global self-consistent, hierarchical, high-resolution geography database GIS shapefiles (Wessel and Smith, 1996). These regions were subdivided into ecofloristic zones defined by the Food and Agriculture Organization (FAO; Fig. S3; Ruesch and Gibbs, 2008, http://cdiac.ornl.gov/epubs/ndp/global_carbon/carbon_documentation.html).

The Siberian region has the highest fraction of trajectories to the Lomonosovfonna site, accounting for 39%, 15%, and 38% of the trajectories in spring, summer, and fall from 2006-2015 CE, respectively. Siberian trajectories were most commonly from boreal tundra woodlands, boreal conifer forests, and boreal mountain systems (Fig. S4; Table S1). Fewer than 3% of the trajectories transected other Siberian ecofloristic zones. Europe contributed fewer than 11% of the trajectories arriving at the site in any season. Those trajectories most commonly encountered boreal coniferous forests, boreal mountain systems, and temperate oceanic forests (Fig. S5; Table S1). Pollen species in the Lomonosovfonna ice core covering the past 150 years drilled

in 1997 match northern boreal taxa from Fennoscandia (Hicks and Isaksson, 2006). Biomass burning aerosols from Eastern European agricultural fires in 2006 reached Svalbard within a few days (Stohl et al., 2007). Other European ecofloristic zones contributed to fewer than 5% of the trajectories in any season. North America contributed fewer than 4% of the trajectories for any season. This analysis does not rule out contributions from North America, but it does suggest that such input would likely require considerably longer atmospheric transport times.

2.3 Ice core sample preparation and analysis

For this study, we resampled discrete ice core samples previously analyzed for major ions (Wendl et al., 2015). The original ice core samples were 1.8x1.9 cm in cross section and 3-4 cm long, melted and stored frozen in polypropylene vials. For analysis of VA and p-HBA, the ice was re-melted, 1 ml was withdrawn from each vial, and the samples from four adjacent vials were combined into one. This resulted in a total of ~~997~~ 993 samples. As discussed below, this sampling procedure resulted in decreasing temporal resolution with increasing depth from subannual samples at the surface to about 2-year samples at the bottom of the core.

VA and p-HBA in the ice core samples were measured using anion exchange chromatographic separation and tandem mass spectrometric detection in negative ion mode with an electrospray ionization source (IC-ESI-MS/MS). The analytical methods and standards used in this study are described in detail by Grieman et al. (2017). The experimental system consisted of a Dionex AS-AP autosampler, ICS-2100 integrated reagent-free ion chromatograph, and ThermoFinnigan TSQ Quantum triple quadrupole mass spectrometer. VA was detected at two mass transitions (m/z 167→108 and m/z 167→152) and p-HBA was detected at m/z 137→93.

Limits of detection for single measurements were estimated using three times the standard deviation of the MilliQ water blank. The limits of detection for the VA m/z 167→108 and 167→152 transitions were ~~0.006 and~~ 0.010 and 0.006 ppb (n = 80), respectively. The limit of detection for p-HBA was 0.012 ppb (n = 80). The mass spectrometer signals for VA at the two mass transitions were highly correlated and either mass transition can be used to measure ice core VA (Fig. S6). Data from the m/z 167→152 transition is reported here because of the slightly better detection limit.

3 Results and Discussion

3.1 Analytical results and data processing

In this study, 993 samples were analysed for VA and p-HBA (Fig. ~~2~~2). VA and p-HBA levels range from below detection to 0.2 and 0.07 ppb, respectively. A substantial fraction of the VA and p-HBA data (67% and 58%, respectively) ~~are below~~ is below the limits of detection. Data below the limits of detection are reported as 0.5 times the limit of detection (0.003 ppb for VA and ~~.006~~ 0.006 ppb for p-HBA). Smoothing of the data was carried out using ~~both~~ time bin averaging (10, 40, and 100-year)~~and LOESS smoothing. Both~~ , LOESS smoothing, and moving averages. All smoothing treatments reveal similar multi-decadal and centennial-scale features in the records and the choice of smoothing technique does not influence the interpretation of

the data (Fig. S7~~). Frequency~~ ; Fig S8). Geometric means and standard deviations of the transformed data were used for all statistics because frequency distributions of the data show skewness towards lower concentrations~~and geometric means and standard deviations were used in time bin averaging~~. Time-averaging compensates for the decrease in frequency of sampling with depth in the core due to layer thinning.

3.2 The Lomonosovfonna vanillic and p-hydroxybenzoic acid time series

The Lomonosovfonna VA and p-HBA time series exhibit variability on a wide range of time scales. There is abundant annual to decadal variability in both records. The amplitude of individual peaks in the raw data is roughly similar across the whole record for both compounds, ranging from 0.1-1.2 ppb for VA and 0.1-0.8 for p-HBA (Fig. 2). The peaks appear to be of longer duration during the older portions of both records. Both of these aspects of the raw data are likely artifacts due to the combined effect of annual layer thinning with depth and the sampling strategy of analyzing individual ice core samples of constant thickness (12-16 cm). The time span integrated by individual samples ranged from 1.7 years near the bottom of the core, to 0.5 years at mid-depth (∼80 m), to 0.07 years near the top (Fig. S1). This thinning effect is eliminated when the data are time bin-averaged. Peaks in the 10-year bin-averaged records are roughly similar in duration across the whole record (Fig. 3). In the bin-averaged data, the magnitudes of the peaks are no longer constant across the record. For VA, the two early peaks (1250-1280 and 1360-1390 CE) are much larger than all subsequent peaks. p-HBA exhibits three major multi-decadal peaks. One is simultaneous with the early VA peak (1250-1280 CE) and the others occur from 1520-1570 and 1610-1640 CE.

Both compounds exhibit long-term decreasing trends over the 800-year record, as illustrated by the 40-year bin averaged data (Fig 3). 40-year bin-averaged VA levels decline by about a factor of three over the first half of the record (1200-1600 CE), then remain relatively steady for the remainder of the record. It is possible that the decline in VA continued after 1600 CE but much of the data after this time is near or below detection. 40-year bin-averaged p-HBA levels decline by about a factor of two over the whole 800-year record.

Centennial scale variability is observed as pronounced maxima early in the record (1300-1500 CE), as illustrated by the 40-year bin averages (Fig. 3). There are hints of continued centennial scale variability in VA in the remainder of the record. Centennial scale variability is evident throughout the p-HBA record, with maxima coinciding with the VA maxima early on and with additional maxima in the 1500's, 1600's, and 1800's.

The 20th century levels of VA and p-HBA are not anomalous relative to the rest of the ice core record. VA exhibits a slight increase after 1970 and the largest single peak in the record occurs from 2000-2008 CE (Fig. 4). p-HBA levels also appear to increase after 1970, although to a lesser degree than VA. The 2000-2008 period is slightly elevated in p-HBA but not to the extent observed in VA. The samples from 1997-2009 CE are within the firn layer. It is possible that firn samples could be contaminated with biomass burning aerosols during handling in the field but we have no reason to suspect that the ~~methoxy~~ aromatic acids in these samples are influenced by contamination. We have not observed laboratory contamination for these compounds as a significant issue in our laboratory.

Wavelet analysis was used to illustrate temporal variations in the spectral content of the signals. Lomonosovfonna VA and p-HBA time series exhibit non-stationary periodic variability, meaning that the spectral characteristics vary with time (Fig. ~~S8~~S9).

3.3 Potential for post depositional modification of VA and p-HBA

There have been no field studies of atmosphere/snow interactions for aromatic acids like VA and p-HBA, so little is known about postdepositional effects. Three types of effects should be considered: 1) revolatilization after deposition to the snowpack, 2) vertical redistribution associated with melting, percolation, and refreezing, and 3) degradation due to chemical or microbiological processes. All of these effects would likely occur to a greater extent at relatively warm sites like Lomonosovfonna (mean annual temperature -12.5°C), and during warmer periods like the Medieval Climate Anomaly or the 20th century. Redistribution associated with melt layers has been discussed in detail for other ions (Wendl et al., 2015), and one would expect that the influence of these processes on aromatic acids would be similar. Wendl et al. (2015) used principal component analysis to determine that melt layers did not have a major influence on the distribution of ions on decadal timescales. Finally, the VA and p-HBA data from Lomonosovfonna and Akademii Nauk argue against chemical degradation as an important process, since there is clearly no monotonic decrease in VA or p-HBA levels downcore.

The fact that VA and p-HBA are commonly observed in atmospheric aerosols, even after long distance transport, suggests that the volatility of these compounds in aerosols might be considerably lower than that of the pure substance (Simoneit and Elias, 2000; Simone The vapor pressures for VA and p-HBA are 0.0023 pa and 2.5 x 10^{-5} pa (https://chem.nlm.nih.gov/chemidplus/rn/121-34-6 Jones, 1960) at 25°C, respectively. Ionic interactions with salts or hydrophobic interactions with soot or complex organics may stabilize aromatic acids in aerosols or snow. Laboratory and aerosol field studies have demonstrated reduced volatility of low molecular weight organic acids (relative to the vapor pressure of the pure compound) due to interaction with cations derived from seasalt or other sources, but this effect has not been studied for aromatic acids (Häkkinen et al., 2014; Laskin et al., 2012).

If revolatilization of aromatic acids from the snowpack does occur, one might expect loss to be enhanced in ice acidified by high levels of nitrate and sulfate from volcanic or pollutant inputs. There is no obvious evidence that acidification is a dominant control on VA or p-HBA levels in the ice core (Fig. S10). It is particularly notable that VA and p-HBA levels are not anomalously low during the twentieth century, when ice core sulfate and nitrate levels increased several-fold compared to the preindustrial era (Fig. S10; Fig. S11). Based on the ice core signals alone, we conclude that re-volatilization does not appear to be the predominant factor controlling ice core aromatic acid levels, although this cannot be ruled out. Further investigation of this issue is needed.

3.4 Relationship to ammonium record

Here we compare the variability of Lomonosovfonna VA and p-HBA to the previously published ammonium record from the same ice core (Wendl et al., 2015). That study concluded that prior biogenic sources were the major contributor to ammonium in the ice core prior to the mid-1800's, and agriculture became a major source during the 20th century. Prior studies have suggested that episodic ammonium peaks in ice cores represent a fire signal, while longer-term variability reflects the biogenic

signal (Fischer et al., 2015; Legrand et al., 2016). Following Fischer et al. (2015), we used singular spectrum analysis (SSA) to decompose the Lomonosovfonna VA, p-HBA, and ammonium records into these two components.

The analysis was done by computing 30 principle components (PC's) using 3-year bin averaged data for VA, p-HBA, and ammonium (Wendl et al., 2015). The low frequency component (PC-1) of the ammonium record shows little similarity to PC-1 for either of the organic acids. VA and p-HBA exhibit decreasing trends over the record while ammonium increases (Fig. 5). To compare the higher frequency components, we used a peak detection method (Higuera et al., 2010). This was done by summing PC's 2-30 and counting the frequency of peaks above a threshold (75th percentile) in a 40-year moving window. The resulting signals for VA and p-HBA exhibit centennial-scale variability that is consistent with that obtained from bin-averaging (Fig. 3) and ammonium exhibits similar variability on these time scales. The correlation coefficient between VA-ammonium and p-HBA-ammonium was computed from the peak frequency data using a 200-year moving window. The 95% confidence interval for these correlation coefficients are shown in Fig. 5. Based on this analysis, ammonium and VA are positively correlated for three time periods (1300-1450; 1675-1725; post-1880). Ammonium and p-HBA exhibit positive correlations for two time periods (1425-1650; 1825-1875). Interestingly, the positive correlations for ammonium with VA and with p-HBA occur at different intervals. The fact that some extended periods of correlation between VA, p-HBA, and ammonium are present in the Lomonosovfonna record suggests that there may be a fire-derived contribution to the ammonium signal in this ice core. However, the relationships are obviously complex and worthy of further study.

3.5 Relationship to sedimentary charcoal records

Sedimentary charcoal records in the Global Charcoal Database (GCD) from Siberia (50-70°N, 50-150°E) and Fennoscandia (50-70°N, 0-50°E) were analyzed using the paleofire R package (GCD: Blarquez et al., 2014). Only 3 of the 12 Siberian records in the GCD have sufficient data from 1200-2000 CE for comparison to the Lomonosvfonna ice core record. These regions are Chai-ku Lake in eastern Siberia, and Zagas Nuur and Lake Teletskoye in southern Siberia. The Siberian region as a whole is therefore not well-represented. Six of the 19 Fennoscandian records in the GCD have enough data from 1200-2000 CE for comparison to the Lomonosovfonna ice core record. Siberia and Fennoscandia are primarily boreal tundra woodlands, boreal conifer forests, and boreal mountain systems (Fig. S3; Ruesch and Gibbs, 2008). One important caveat to this comparison is that the dating of sedimentary charcoal records is often based on linear interpolations between a few ^{14}C ages. Hence their age scales are typically less well-constrained than Lomonosovfonna or other ice cores.

Four of the six records from Fennoscandia exhibit increased charcoal influx from 1200-1400 CE (Fig. S12; Blarquez et al., 2014). Lomosovfonna VA and p-HBA are both elevated during this period. Three of the six charcoal records are elevated around 1600 CE when Lomonosovfonna p-HBA is also elevated. Two of the records also show a long-term decline from 1200-2000 CE similar to the Lomosovfonna VA and p-HBA records. Two of the Siberian records exhibited increased charcoal influx from 1200-1600 CE relative to 1600 CE to present (Fig. S13). The Lomonosovfonna VA and p-HBA are also higher early in the record. The Fennoscandian records are clearly most similar to the Svalbard ice core record, but the database is too limited to determine definitively the srouce region for the VA and the p-HBA in the Lomonosovfonna ice core from so few charcoal records.

3.6 Comparison between Svalbard and Siberian ice core records of vanillic acid and p-hydroxybenzoic acid

The only other millennial scale ice core record of VA and p-HBA is the Akademii Nauk ice core from the Severnaya Zemlya Archipelago in the Arctic Ocean north of central Siberia (Grieman et al., 2017; Fritzsche et al., 2002). The Akademii Nauk ice core covers a considerably larger time range than Lomonsovfonna, extending over the past 2600 years. Here we discuss only the period of temporal overlap between the two ice cores (1200-2000 CE).

The two ice core records exhibit similar trends and levels during the early part of the record (1220-1400 CE; Fig. ~~S9~~S14). During this period, Lomonosovfonna exhibits declining levels of both aromatic acids. In the Akademii Nauk core, this period represents the tailing end of an earlier peak in both aromatic acids with a maximum around 1200 CE. The two cores diverge markedly after 1400 CE for the remainder of the records (Fig. ~~5~~6). Akademii Nauk VA exhibits a period of highly elevated levels from 1460-1660 CE. During this period, Akademii Nauk VA reaches levels more than an order of magnitude above those of Lomonosovfonna VA. Akademii Nauk p-HBA exhibits a period of elevated levels from 1460-1550 and 1780-1860 CE. There are multi-decadal peaks in p-HBA in the Lomonosovfonna record that overlap in time with the large Akademii Nauk VA peaks, although not nearly as large in amplitude or duration. Interestingly, these peaks do not appear at all in the Lomonosovfonna VA record.

~~Back~~ 10-day back trajectories were computed for the Akademii Nauk site using the same methods as those described above from 2006-2015 CE (section 2.2; Grieman et al., 2017). ~~Both~~ The trajectories show that both of the Lomonosovfonna and Akademii Nauk sites are influenced by air masses transecting Eurasian forested regions (Fig. ~~6~~7; Table S1). The ~~highest percentages~~ largest fraction of trajectories transect Siberian boreal tundra woodland, boreal coniferous forests, and boreal mountain systems for both ice core sites, particularly in the summer and fall. Given this similar transport pattern, we would have expected the two large multi-century peaks in Siberian aromatic acids after 1400 CE to be exhibited in the Lomonosovfonna record as well. The sharp divergence between the two records around 1400 CE and the subsequent dramatic increase in aromatic acids only in the Siberian ice core suggest a change in transport patterns to the sites after 1400 CE. The fraction of back trajectories transecting vegetated regions of Siberia for Akademii Nauk were about twice that for Lomonosovfonna~~due to the shorter distance~~. Conversely, trajectories from European forests comprise a smaller contribution to Akademii Nauk than to Lomonosovfonna. Air masses from European regions are more likely to reach the Lomonsovfonna site than the Akademii Nauk site. We speculate that the divergence between the two ice cores reflects a shift in large-scale atmospheric circulation patterns, as discussed below.

3.7 Relationship to atmospheric circulation and climate

The general climate context for the last millennium is Late Holocene cooling, with superimposed centennial scale climate variability associated with the Medieval Climate Anomaly (MCA, 950-1250 CE), the Little Ice Age (LIA, 1400-1700 CE), and the twentieth century warming (PAGES 2k Consortium, 2013; Lamb, 1965; Mann et al., 2009). Svalbard δ^{18}O ice core records show that cooling continued in the region through the 19th century (Divine et al., 2011). Divine et al. (2011) suggest that the extended LIA at Svalbard could reflect the climatic influence of regional sea ice conditions. In that case, the extended LIA was

probably not characteristic of the biomass burning source regions in Europe and Siberia influencing the Lomonosovfonna ice core.

For recent decades, increased burning of wildfires is generally associated with higher summer temperatures (Flannigan et al., 2009). On that basis alone, one might expect to see a long term decrease in aromatic acid signals over the last millennium, and that is generally the case for both VA and p-HBA in the Lomonosovfonna ice core. However, on multi-century and centennial time scales, the variability in the aromatic acids in the Lomonosovfonna ice core is also large and somewhat complex. Both VA and p-HBA levels were high during the MCA. VA declines into the LIA. p-HBA exhibits elevated levels during the latter half of the LIA but VA does not (Fig. ~~7~~8). This dissimilarity could be due to a shift in ~~the biomass burning source region~~ spatial patterns of either biomass burning or atmospheric transport after 1400 CE.

It seems likely that regional changes in burning proxies on multi-century and centennial time scales are strongly linked to changes in large scale atmospheric circulation and the resulting impacts on regional climate and atmospheric transport. For the source regions influencing the Svalbard Lomonosovfonna ice core, one might expect that changes in the North Atlantic Oscillation (NAO) might play an important role. The NAO is a major mode of climate variability in the North Atlantic region, characterized by changes in the pressure gradient between the Icelandic Low and the Azores High during winter months (Hurrell et al., 2001). Strong pressure gradients (positive NAO index) are associated with strong zonal flow, enhanced westerlies transporting warm air to Europe, increased precipitation in northwest Europe, and decreased precipitation in southern Europe (Trouet et al., 2009). Weaker pressure gradients (negative NAO index) are associated with stronger meridional flow and cooling of the North Atlantic region (Trouet et al., 2012). Proxy NAO records have been developed from variations in wintertime seasalt sodium in the GISP2 ice core, from Moroccan tree-rings and speleothem records in Scotland, and from lake sediments in southwestern Greenland (Meeker and Mayewski, 2002; Trouet et al., 2009; Olsen et al., 2012).

The proxy NAO records show a marked change in phase at the onset of the LIA (around 1400 CE) from several hundred years of positive NAO index to a more negative and variable NAO state that continued throughout and after the LIA (Fig. ~~7~~8). The Lomonosovfonna oxygen isotope (δ^{18}O) record shows a cooling trend at this time, consistent with the NAO shift (Wendl et al., 2015). The change in NAO behaviour at this time was accompanied by a decline in VA in the Lomonosovfonna record, a decline in the VA/HBA ratio, and a sudden divergence between the Lomonosovfonna and Akademii Nauk ice cores (1400 CE). We ~~propose that a reorganization~~ suggest that a change of high latitude northern hemisphere atmospheric circulation patterns occurred at this time, resulting in 1) a cooler, wetter northern Europe with less burning, and 2) reduced zonal transport, resulting in 'decoupling' of the two ice core signals. Central Siberian burning likely increased at this time, as evidenced by sharply increased aromatic acids in the Akademii Nauk ice core. The Siberian ice core signals are similar in timing to changes in the strength of the Asian monsoon, as recorded in speleothem proxy records (Grieman et al., 2017; Wang et al., 2005). We speculate that during the LIA, central Siberia was influenced primarily by conditions in the Pacific rather than the Atlantic Ocean.

The summertime NAO (SNAO) is defined as the leading mode of July–August sea level pressure variability in the North Atlantic sector (Folland et al., 2009; Efthymiadis et al., 2011). The SNAO affects temperatures, precipitation, and cloudiness in Europe during summer, and one might expect that variations in burning are even more directly linked to the SNAO than

the NAO. The SNAO has a slightly different spatial pattern than the NAO, with a relatively small Arctic node and a southern node over northwestern Europe. The positive (negative) mode of the SNAO is characterized by ~~warmer (cooler) summer temperatures over the United Kingdom and lower (higher) precipitation over~~ a warmer and drier (cooler, wetter) northern Europe (Linderholm et al., 2008; Folland et al., 2009). The influence of the SNAO extends to central Asia, and so could influence both major source regions for the Lomonosovfonna ice core. ~~Any relationship between SNAOvariability and the Lomonosovfonna record could be due to 1) the effect of the SNAO on climate, which in turn affects biomass burning, or~~

In order to illustrate the possible influence of the SNAO, we compared back trajectories from the Lomonosovfonna site for recent periods when the SNAO index was positive (1970-1979 CE, mean SNAO index: 6.3) and negative (1948-1957 CE; mean SNAO index: -2.0) (Folland et al., 2009). Figure 9 shows the major spatial clusters of 10-day air mass back trajectories for each time period (computed using Hysplit) superimposed on the sea level pressure (SLP) anomalies relative to mean SLP from 1948-2017. The high SNAO period is characterized by 1) high pressure over Scandinavia, favoring drier conditions, and 2) ~~changes~~ trajectories generally originating at lower latitudes, with a larger fraction of transport from Scandinavia. These results suggest that SNAO-driven variability in atmospheric transport could contribute to variability in burning signals in the Lomonosovfonna record.

SNAO variability has been reconstructed for the past 500 years using historical documents and tree rings (Linderholm et al., 2008, 2009, 2013; Luterbacher et al., 2001). The SNAO record is primarily negative over the past 500 years, with brief positive excursions until the start of the 20th century when it shifted into its positive phase (Linderholm et al., 2009). The long-term trends in the SNAO and NAO reconstructions are generally similar, and there are some common features on centennial time scales ~~(Fig. 7; Trouet et al., 2009)~~(Fig. 8; Trouet et al., 2009). Both NAO and SNAO records exhibit a positive excursion from 1500-1650 CE, during a period of elevated p-HBA in Lomonosovfonna. After 1400 CE, VA remains low and does not show similar ~~timing~~ variability to p-HBA. This incoherence between the records could be due to the change in atmospheric circulation patterns after 1400 CE when the Svalbard and Siberia ice core records diverge.

~~In order to explore the possible influence of the SNAO on transport patterns, we compared back trajectories from the Lomonosovfonna site for recent periods when the SNAO index was positive (1970-1979 CE)and negative (1948-1957 CE) (Folland et al., 2009). The average observed SNAO index from 1970-1979 and 1948-1957 CE are 6.3 and -2.0, respectively. Transport from Siberian boreal coniferous forests and mountain systems is slightly higher in the spring and fall and slightly lower in the summer than when the SNAO is negative relative to when it is positive (Fig. 8). Transport from European coniferous forests and mountain systems was slightly higher in the spring, much higher in the summer, and lower in the fall during the positive phase of the SNAO compared to the negative phase. These results suggest that SNAO-driven variability in atmospheric transport could contribute to variability in burning signals in the Lomonosovfonna record.~~

3.8 Lomonosovfonna ice core VA/p-HBA ratios

~~In general, laboratory studies indicate that grasses and trees yield roughly similar emission factors for many organic compounds~~ The mean VA/p-HBA ratio for the Lomonosovfonna ice core using the 10-year bin averages of each record is 0.40±0.25 (n=79). Both compounds are produced during the smoldering phase of burning (Akagi et al., 2011; Legrand et al., 2016; Simoneit, 2002) and

both are produced from combustion of major boreal forest tree species. Short term changes in the ratio most likely reflect the changing contributions from various source regions with different ecosystems. Longer term changes in the ratio could reflect changes in ecology/biogeography (i.e. ~~grams emitted per gram of fuel burned). While biomass in forests far exceeds that in grasslands, forest fire recurrence intervals are much longer (van der Werf et al., 2010). Consequently, forests and grasslands make comparable contributions to biomass burning emissions (van der Werf et al., 2010)~~shifts between conifer and broadleaf forests or grasslands) or changes in atmospheric transport patterns. As noted earlier, analysis of back trajectories suggests that boreal forests are the principle source regions for this ice core, with minor contributions from tundra and temperate forests.

~~Laboratory combustion studies show a wide range in the chemical composition and relative abundance of the various organic compounds generated during biomass burning. Boreal forests in Siberia consist primarily of larch, pine, spruce, and fir tree genera (Soja et al., 2007). We are not aware of~~ The range of VA/p-HBA ratios observed in the Lomonosovfonna ice core is consistent with the laboratory combustion studies ~~using the actual species comprising Siberian boreal forests, but~~ of boreal forest tree species. Combustion studies have been conducted on several conifers characteristic of North American and European boreal forests~~have been studied.~~ . North American conifer (Lodgepole pine, Sitka spruce, Douglas fir, and Mountain hemlock) combustion yielded VA~~and p-HBA emissions in the range of 1.8-5.9 μg/g conifer fuel burned and VA/~~p-HBA weight ratios ranging from 0.40-0.99 (Oros and Simoneit, 2001a) ~~. Some types of~~ (Table S2, Supplemental Material). Specific North American conifers produce only one of the two ~~aromatic acids~~compounds. For example, Eastern White pine produced only VA, and Noble fir produced only p-HBA (Oros and Simoneit, 2001a). European ~~pine, European pine with green needles, European spruce with green needles, and peat from western Germany~~ conifers and peat burning produced VA/p-HBA ~~ratios (μg/g of fuel burned: μg/g of fuel burned)~~ weight ratios ranging from 0.07-8.75 ~~(14.0:1.6, 0.6:8.1, 2.6:38.0, and 3.0:36.0, respectively; Iinuma et al., 200~~ ~~Tundra grass from the Yukon Territories in Canada produced 1.7 μg p-HBA~~(Iinuma et al., 2007). Combustion of a German peat sample yielded a low VA/~~g fuel burned, but VA was not detected (Oros et al., 2006).~~

~~The mean VA /~~p-HBA ~~ratio for the Lomonosovfonna ice core using the 10-year bin averages of each record is 0.40 $\pm$ 0.25 (n=79). The~~ ratio of 0.08 (Iinuma et al., 2007; Oros et al., 2006). Combustion of a tundra grass sample from the Canadian Yukon Territories produced p-HBA only, but at rates 1000-fold less than conifers (Oros et al., 2006). Deciduous tree species produced roughly 1000-fold more VA than conifers (mg VA/kg fuel burned), and deciduous species did not produce detectable levels of p-HBA ~~ratio is relatively high early in the record, decreasing by a factor of about two from 1200-1500 CE (Fig. 3). The ratio remains low until about 1850 CE, and then increases through the remainder of the record with a sharp increase at 2000 CE. Early in the record, elevated~~ (Oros and Simoneit, 2001a, b). Thus even a small fraction of air mass trajectories from temperate forests could influence the VA/p-HBA ~~ratios are observed in the two major VA spikes around 1270 and 1370 CE. The first VA peak is also a clear peak in p-HBA concentration, but the second VA peak, which is weaker than the first peak, is not evident as a peak in the p-HBA record. From 1540-1620 CE, there is a p-HBA peak without a corresponding peak in the VArecord.~~ ratio.

~~The VA~~We are not aware of laboratory combustion studies of the actual species comprising Siberian forests or tundra. This is a major gap in the knowledge base needed to interpret Arctic ice core data. Similarly, very few studies to date have reported VA/p-HBA ratios for ambient Arctic aerosols. Fu et al. (2009) reported ratios ranging from 0.16-2.2 in weekly aerosol

samples collected at Alert, covering the range observed in the ~~Lomonosovfonna ice coreare generally consistent with the laboratory combustion results from boreal forest tree species. Both VA and p-HBA are emitted by the pyrolysis of lignin during the smolering stage of a fire (Akagi et al., 2011; Legrand et al., 2016; Simoneit, 2002). A change in the burning conditions is therefore unlikely to alter the VA/p-HBA ratio~~ice core. ~~The~~

There are significant long-term ~~trends in the VA/p-HBA ratio presumably reflect changes in the relative contributions of fuel types or changes in atmospheric transport. In addition to the long-term trends, there are some notable short-term excursions. It is interesting that these decadal or multi-decadal events all appear as transient increases in the~~ changes in the Lomonosovfonna VA/p-HBA ~~ratio and there are no equivalent decreases of similar magnitude. These events are too brief to represent major ecological changes, but too long to represent single events. They could reflect unusual events such as regional prolonged droughts, or multiyear tundra or boreal peat fires. The~~ ratio over time. The ratio is relatively high during the MCA (0.8), decreases by a factor of two from 1200-1400 CE, remains low through the LIA until around 1800 CE (Fig. 3). There is also an increase in VA/p-HBA ~~ratio increase~~ after 1800~~is likely due to the gradual decrease in the p-HBA baseline. As noted earlier, the VA baseline appears level after 1800 but is at or near~~ , although VA is close to the detection limit ~~. Hence, the apparent change~~ and the uncertainty in the ratio is consequently large. Interestingly, the changes in the VA/p-HBA ratio ~~after 1800 CE may be an artifact of our inability to resolve trends in the very low levels of VA.~~

3.9 ~~Potential for post depositional modification of VA and p-HBA~~

~~There have been no field studies of atmosphere~~broadly mirror changes in the phase of the paleoreconstructions of the NAO and SNAO (Fig. 8). One might speculate that the associated changes in climate and transport mentioned earlier contribute to the variations in the VA/~~snow interactions for methoxy aromatic acids like VA and~~ p-HBA ~~, so little is known about postdepositional effects. Three types of effects should be considered: 1) revolatilization after deposition to the snowpack, 2) vertical redistribution associated with melting, percolation, and refreezing, and 3) degradation associated due to chemical or microbiological processes. All three of these effects would likely occur to a greater extent at relatively warm sites like Lomonosovfonna (mean annual temperature -12.5°C)than at cold sites, and during warmer periods like the 20th century, than during the LIA. Redistribution associated with melt layers has been discussed in detail for other ions (Wendl et al., 2015), and one would expect that the influence of these processes on methoxy aromatic acids would be similar. Wendl et al. (2015) used principal component analysis to determine that melt layers did not have a major influence on the distribution of ions on decadal timescales. The VA and p-HBA data from Lomonosovfonna and Akademii Nauk argue against chemical degradation as an important process, since there is clearly no monotonic decrease in VA or p-HBA levels downcore~~ratio but the specific causes are not understood at this time.

~~The fact that VA and p-HBA are commonly observed in atmospheric aerosols, even after long distance transport, suggests that the volatility of these compounds in aerosols might be considerably lower than that of the pure substance. The vapor pressures for VAand~~ There are several multi-decadal excursions in the VA/p-HBA ~~are 0.0023 pa and 2.5 x 10^{-5} pa (https://chem.nlm.nih.gov/chemidp 25°C, respectively. Ionic interactions with salts or hydrophobic interactions with soot or complex organics may stabilize aromatic acids in aerosols or snow. Laboratory and aerosol field studies have demonstrated reduced volatility of low molecular~~

weight organic acids (relative to the vapor pressure of the pure compound) due to interaction with cations derived from seasalt or other sources, but this effect has not been studied for aromatic acids (Häkkinen et al., 2014; Laskin et al., 2012).

If re-volatilization of methoxy aromatic acids from the snowpack does occur, one might expect loss to be enhanced in ice acidified by high levels of nitrate and sulfate from either volcanic or pollutant inputs. There is no obvious evidence that acidification is a dominant control on VA or p-HBA levels in the ice core (Fig. S10). It is particularly notable that VA ratio. Ratios greater than 1 occur in the VA peaks around 1270 and 1370 CE. The second of these peaks is a notable increase in VA, with no corresponding peak in p-HBA. Conversely, around 1540 and 1620 CE, there are p-HBA levels are not anomalously low during the twentieth century, when ice core sulfate and nitrate levels increased several-fold compared to the preindustrial era (Fig. S10; Fig. S11). Based on the ice core signals alone, we conclude that re-volatilization does not appear to be the predominant factor controlling ice core methoxy aromatic acid levels, although this cannot be ruled out. Further investigation of this issue is neededpeaks without a corresponding peak in the VA record. These events are probably too short to represent ecological changes, but too long to represent single fire events or seasons. Such events are worthy of further investigation.

4 Conclusions

The Lomonosovfonna ice core record shows that the methoxy pyrogenic aromatic acids, vanillic acid and para-hydroxybenzoic acid, are present in Arctic ice and preserved on millennial time scales. The observed temporal variability of these signals contains should contain information about the history of high latitude burning in Northern Europe and Siberia. VA and p-HBA are both high elevated from 1200-1400 CE and decline until the Little Ice Age. On centennial Paleoclimate proxy records indicate that this transition coincides with a shift in the North Atlantic Oscillation from positive to a more negative state, but the causal basis for a relationship is not established.

On centennial and shorter timescales, the compounds two acids exhibit some notable differences. For example, the two largest peaks in the p-HBA record around 1600 CE are not part of present in the VA record. This difference in the records could be due to a change in the vegetation type burned or atmospheric transport pattern to the ice core site. The highest Conversely, elevated levels of VA exhibited from 2000-2008 CE are not shown present in the p-HBA record. Further studies of VA levels in snow pits near the ice core site should be conducted to confirm these recent high levels of VA. It should be noted that these records have not been validated or calibrated by comparison to instrumental or satellite trends in biomass burning Such anomalies are intriguing in that they suggest significant changes in either burning patterns or atmospheric transport. Further studies of the variability of these compounds in ice cores covering the instrumental and satellite eras should be conducted. Shallow ice core measurements of these compounds covering over the instrumental period across the Arctic are needed.

The two millennial scale ice cores analysed for these compounds to date, Lomonosovfonna and Akademii Nauk, show intriguing similarity between the Svalbard and Siberian records at the end of the Medieval Climate Anomaly (1200-1400 CE) but dramatic differences for most of the past millennium. Such differences are surprising given that air mass trajectories based on reanalysis data indicate considerable overlap in source areas for the two ice cores. It seems that there must exist a large-scale

dynamical explanation of the regional/temporal trends in these and other proxy fire records. Developing a unified interpretation of these signals will require further work.

5 Data availability

The data reported in this manuscript will be submitted to the NSF Artic Data Center (http://arcticdata.io/) before publication.

Author contributions. Mackenzie Grieman, Murat Aydin, and Eric Saltzman developed the analytical method. Mackenzie Grieman combined and measured the ice core melt samples used in this study and processed the data. Mackenzie Grieman and Eric Saltzman wrote the manuscript. Margit Schwikowski and her team drilled and processed the ice core, provided samples, developed the depth-age scale, and provided comments on the manuscript. Elisabeth Isaksson initiated the Lomonosovfonna ice core drilling project, was responsible for field logistics, and provided comments on the manuscript. Murat Aydin provided comments on the manuscript.

Competing interests. The authors declare that they have no conflicts of interest.

Acknowledgements. NCEP/NCAR reanalysis data were accessed from: ftp://arlftp.arlhq.noaa.gov/pub/archives/reanalysis. We would like to acknowledge S. Brütsch and M. Sigl for assistance with collecting ice core melt samples, C. McCormick for help with instrument maintenance, and T. Sutterley and A. Payne for help with coding. We would also like to acknowledge research support by a generous donation from the Jenkins Family to the Department of Earth System Science, University of California, Irvine. Funding was also provided by the National Science Foundation (ANT-0839122; PLR-1142517) and by the NSF Independent Research/Development program. Wavelet software was provided by C. Torrence and G. Compo (http://paos.colorado.edu/research/wavelets/; Torrence and Compo, 1998). The Global Charcoal Database was accessed at: http://gpwg.paleofire.org.

References

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmospheric Chemistry and Physics, 11, 4039–4072, doi:10.5194/acp-11-4039-2011, 2011.

Beaudon, E., Moore, J. C., Martma, T., Pohjola, V. A., Van De Wal, R. S., Kohler, J., and Isaksson, E.: Lomonosovfonna and Holtedahlfonna ice cores reveal eastwest disparities of the Spitsbergen environment since AD 1700, Journal of Glaciology, 59, 1069–1083, doi:10.3189/2013JoG12J203, 2013.

Blarquez, O., Vannière, B., Marlon, J. R., Daniau, A.-L., Power, M. J., Brewer, S., and Bartlein, P. J.: Paleofire: An R package to analyse sedimentary charcoal records from the Global Charcoal Database to reconstruct past biomass burning, Computers and Geosciences, 72, 255 – 261, doi:10.1016/j.cageo.2014.07.020, 2014.

Bouwman, A. F., Lee, D. S., Asman, W. A. H., Dentener, F. J., Van Der Hoek, K. W., and Olivier, J. G. J.: A global high-resolution emission inventory for ammonia, Global Biogeochemical Cycles, 11, 561–587, doi:10.1029/97GB02266, 1997.

Bowman, D. M., Balch, J. K., Artaxo, P., Bond, W. J., Carlson, J. M., Cochrane, M. A., D'Antonio, C. M., DeFries, R. S., Doyle, J. C., Harrison, S. P., et al.: Fire in the Earth system, science, 324, 481–484, doi:10.1126/science.1163886, 2009.

Chapin, F. S., Mcguire, A. D., Randerson, J., Pielke, R., Baldocchi, D., Hobbie, S. E., Roulet, N., Eugster, W., Kasischke, E., Rastetter, E. B., Zimov, S. A., and Running, S. W.: Arctic and boreal ecosystems of western North America as components of the climate system, Global Change Biology, 6, 211–223, doi:10.1046/j.1365-2486.2000.06022.x, 2000.

Crutzen, P. J. and Andreae, M. O.: Biomass Burning in the Tropics: Impact on Atmospheric Chemistry and Biogeochemical Cycles, Science, 250, 1669–1678, doi:10.1126/science.250.4988.1669, 1990.

Divine, D., Isaksson, E., Martma, T., Meijer, H. A., Moore, J., Pohjola, V., van de Wal, R. S. W., and Godtliebsen, F.: Thousand years of winter surface air temperature variations in Svalbard and northern Norway reconstructed from ice-core data, Polar Research, 30, 7379, doi:10.3402/polar.v30i0.7379, 2011.

Draxler, R. R., Stunder, B., Rolph, G., and Taylor, A.: HYSPLIT4 user's guide, NOAA Technical Memorandum ERL ARL, 230, 35, 1999.

Efthymiadis, D., Goodess, C., and Jones, P.: Trends in Mediterranean gridded temperature extremes and large-scale circulation influences, Natural Hazards and Earth System Sciences, 11, 2199, doi:10.5194/nhess-11-2199-2011, 2011.

Eichler, A., Brütsch, S., Olivier, S., Papina, T., and Schwikowski, M.: A 750 year ice core record of past biogenic emissions from Siberian boreal forests, Geophysical Research Letters, 36, L18 813, doi:10.1029/2009GL038807, 2009.

Ferretti, D. F., Miller, J. B., White, J. W. C., Etheridge, D. M., Lassey, K. R., Lowe, D. C., Meure, C. M. M., Dreier, M. F., Trudinger, C. M., van Ommen, T. D., and Langenfelds, R. L.: Unexpected Changes to the Global Methane Budget over the Past 2000 Years, Science, 309, 1714–1717, doi:10.1126/science.1115193, 2005.

Fischer, H., Schüpbach, S., Gfeller, G., Bigler, M., Röthlisberger, R., Erhardt, T., Stocker, T. F., Mulvaney, R., and Wolff, E. W.: Millennial changes in North American wildfire and soil activity over the last glacial cycle, Nature geoscience, 8, 723–727, doi:10.1038/ngeo2495, 2015.

Flannigan, M. D., Krawchuk, M. A., de Groot, W. J., Wotton, B. M., and Gowman, L. M.: Implications of changing climate for global wildland fire, International journal of wildland fire, 18, 483–507, doi:10.1071/WF08187, 2009.

Folland, C. K., Knight, J., Linderholm, H. W., Fereday, D., Ineson, S., and Hurrell, J. W.: The summer North Atlantic Oscillation: past, present, and future, Journal of Climate, 22, 1082–1103, doi:10.1175/2008JCLI2459.1, 2009.

Fritzsche, D., Wilhelms, F., Savatyugin, L. M., Pinglot, J. F., Meyer, H., Hubberten, H.-W., and Miller, H.: A new deep ice core from Akademii Nauk ice cap, Severnaya Zemlya, Eurasian Arctic: first results, Annals of Glaciology, 35, 25–28, doi:10.3189/172756402781816645, 2002.

Fu, P., Kawamura, K., and Barrie, L. A.: Photochemical and Other Sources of Organic Compounds in the Canadian High Arctic Aerosol Pollution during Winter–Spring, Environmental Science & Technology, 43, 286–292, doi:10.1021/es803046q, 2009.

Fuhrer, K., Neftel, A., Anklin, M., Staffelbach, T., and Legrand, M.: High-resolution ammonium ice core record covering a complete glacial-interglacial cycle, Journal of Geophysical Research: Atmospheres, 101, 4147–4164, doi:10.1029/95JD02903, 1996.

Gambaro, A., Zangrando, R., Gabrielli, P., Barbante, C., and Cescon, P.: 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, doi:10.1021/ac701655x, 2008.

Grannas, A. M., Shepson, P. B., and Filley, T. R.: Photochemistry and nature of organic matter in Arctic and Antarctic snow, Global Biogeochem. Cycles, 18, GB1006, doi:10.1029/2003GB002133, 2004.

Grieman, M. M., Aydin, M., Fritzsche, D., McConnell, J. R., Opel, T., Sigl, M., and Saltzman, E. S.: Aromatic acids in a Eurasian Arctic ice core: a 2600-year proxy record of biomass burning, Climate of the Past, 13, 395–410, doi:10.5194/cp-13-395-2017, 2017.

Hennigan, C. J., Sullivan, A. P., Collett, J. L., and Robinson, A. L.: Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals, Geophysical Research Letters, 37, L09 806, doi:10.1029/2010GL043088, 2010.

Hessl, A. E.: Pathways for climate change effects on fire: Models, data, and uncertainties, Progress in Physical Geography, 35, 393–407, doi:10.1177/0309133311407654, 2011.

Hicks, S. and Isaksson, E.: Assessing source areas of pollutants from studies of fly ash, charcoal, and pollen from Svalbard snow and ice, Journal of Geophysical Research: Atmospheres, 111, doi:10.1029/2005JD006167, 2006.

Higuera, P. E., Gavin, D. G., Bartlein, P. J., and Hallett, D. J.: Peak detection in sediment–charcoal records: impacts of alternative data analysis methods on fire-history interpretations, International Journal of Wildland Fire, 19, 996–1014, doi:10.1071/WF09134, 2010.

Häkkinen, S. A. K., McNeill, V. F., and Riipinen, I.: Effect of Inorganic Salts on the Volatility of Organic Acids, Environmental Science & Technology, 48, 13 718–13 726, doi:10.1021/es5033103, 2014.

Hoffmann, D., Tilgner, A., Iinuma, Y., and Herrmann, H.: Atmospheric stability of levoglucosan: a detailed laboratory and modeling study., Environmental Science and Technology, 44, doi:10.1021/es902476f, 2010.

Hunter, J. D.: Matplotlib: A 2D Graphics Environment, Computing in Science & Engineering, 9, 90–95, doi:10.1109/MCSE.2007.55, 2007.

Hurrell, J. W., Kushnir, Y., and Visbeck, M.: The North Atlantic Oscillation, Science, 291, 603–605, doi:10.1126/science.1058761, 2001.

Iinuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M. O., Helas, G., Parmar, R., and Herrmann, H.: Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat, Journal of Geophysical Research: Atmospheres, 112, D08 209, doi:10.1029/2006JD007120, 2007.

Jones, A. H.: Sublimation Pressure Data for Organic Compounds., Journal of Chemical and Engineering Data, 5, 196–200, 1960.

Kalnay, E., Kanamitsu, M., Kistler, R., Collins, W., Deaven, D., Gandin, L., Iredell, M., Saha, S., White, G., Woollen, J., Zhu, Y., Leetmaa, A., Reynolds, B., Chelliah, M., Ebisuzaki, W., Higgins, W., Janowiak, J., Mo, K., Ropelewski, C., Wang, J., Jenne, R., and Joseph, D.: The NCEP/NCAR 40-Year Reanalysis Project, Bulletin of the American Meteorological Society, 77, 437–471, 1996.

Kawamura, K., Izawa, Y., Mochida, M., and Shiraiwa, T.: 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, Geochimica et Cosmochimica Acta, 99, doi:10.1016/j.gca.2012.08.006, 2012.

Lamb, H.: The early medieval warm epoch and its sequel, Palaeogeography, Palaeoclimatology, Palaeoecology, 1, 13–37, doi:10.1016/0031-0182(65)90004-0, 1965.

Laskin, A., Moffet, R. C., Gilles, M. K., Fast, J. D., Zaveri, R. A., Wang, B., Nigge, P., and Shutthanandan, J.: Tropospheric chemistry of internally mixed sea salt and organic particles: Surprising reactivity of NaCl with weak organic acids, Journal of Geophysical Research: Atmospheres, 117, D15 302, doi:10.1029/2012JD017743, 2012.

Legrand, M., De Angelis, M., Staffelbach, T., Neftel, A., and Stauffer, B.: Large perturbations of ammonium and organic acids content in the summit-Greenland Ice Core. Fingerprint from forest fires?, Geophysical Research Letters, 19, 473–475, doi:10.1029/91GL03121, 1992.

Legrand, M., McConnell, J., Fischer, H., Wolff, E. W., Preunkert, S., Arienzo, M., Chellman, N., Leuenberger, D., Maselli, O., Place, P., Sigl, M., Schüpbach, S., and Flannigan, M.: Boreal fire records in Northern Hemisphere ice cores: a review, Climate of the Past, 12, 2033–2059, doi:10.5194/cp-12-2033-2016, 2016.

Linderholm, H., Folland, C., and Hurrell, J.: Reconstructing Summer North Atlantic Oscillation (SNAO) variability over the last five centuries, Tree rings in archaeology. Clim Ecol, 6, 8–16, doi:10.2312/GFZ.b103-08056, 2008.

Linderholm, H. W., Folland, C. K., and Walther, A.: A multicentury perspective on the summer North Atlantic Oscillation (SNAO) and drought in the eastern Atlantic Region, Journal of Quaternary Science, 24, 415–425, doi:10.1002/jqs.1261, 2009.

Linderholm, H. W., Seim, A., Ou, T., Jeong, J.-H., Liu, Y., Wang, X., Bao, G., and Folland, C.: Exploring teleconnections between the summer {NAO} (SNAO) and climate in East Asia over the last four centuries – A tree-ring perspective, Dendrochronologia, 31, 297 – 310, doi:10.1016/j.dendro.2012.08.004, 2013.

Luterbacher, J., Xoplaki, E., Dietrich, D., Jones, P. D., Davies, T. D., Portis, D., Gonzalez-Rouco, J. F., von Storch, H., Gyalistras, D., Casty, C., and Wanner, H.: Extending North Atlantic oscillation reconstructions back to 1500, Atmospheric Science Letters, 2, 114–124, doi:10.1006/asle.2002.0047, http://dx.doi.org/10.1006/asle.2002.0047, 2001.

Mack, M. C., Bret-Harte, M. S., Hollingsworth, T. N., Jandt, R. R., Schuur, E. A. G., Shaver, G. R., and Verbyla, D. L.: Carbon loss from an unprecedented Arctic tundra wildfire, Nature, 475, 489–492, doi:10.1038/nature10283, 2011.

Mann, M. E., Zhang, Z., Rutherford, S., Bradley, R. S., Hughes, M. K., Shindell, D., Ammann, C., Faluvegi, G., and Ni, F.: Global Signatures and Dynamical Origins of the Little Ice Age and Medieval Climate Anomaly, Science, 326, 1256–1260, doi:10.1126/science.1177303, 2009.

Marlon, J. R., Bartlein, P. J., Carcaillet, C., Gavin, D. G., Harrison, S. P., Higuera, P. E., Joos, F., Power, M. J., and Prentice, I. C.: Climate and human influences on global biomass burning over the past two millennia, Nature Geosci, 1, 697–702, doi:10.1038/ngeo313, 2008.

Marlon, J. R., Kelly, R., Daniau, A.-L., Vannière, B., Power, M. J., Bartlein, P., Higuera, P., Blarquez, O., Brewer, S., Brücher, T., Feurdean, A., Romera, G. G., Iglesias, V., Maezumi, S. Y., Magi, B., Courtney Mustaphi, C. J., and Zhihai, T.: Reconstructions of biomass burning from sediment-charcoal records to improve data–model comparisons, Biogeosciences, 13, 3225–3244, doi:10.5194/bg-13-3225-2016, 2016.

Mayewski, P. A., Meeker, L. D., Twickler, M. S., Whitlow, S., Yang, Q., Lyons, W. B., and Prentice, M.: Major features and forcing of high-latitude northern hemisphere atmospheric circulation using a 110,000-year-long glaciochemical series, Journal of Geophysical Research: Oceans, 102, 26 345–26 366, doi:10.1029/96JC03365, 1997.

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., and Kahl, J. D. W.: 20th-Century Industrial Black Carbon Emissions Altered Arctic Climate Forcing, Science, 317, 1381–1384, doi:10.1126/science.1144856, 2007.

Meeker, L. D. and Mayewski, P. A.: A 1400-year high-resolution record of atmospheric circulation over the North Atlantic and Asia, The Holocene, 12, 257–266, doi:10.1191/0959683602hl542ft, 2002.

Müller-Tautges, C., Eichler, A., Schwikowski, M., Pezzatti, G. B., Conedera, M., and Hoffmann, T.: Historic records of organic compounds from a high Alpine glacier: influences of biomass burning, anthropogenic emissions, and dust transport, Atmospheric Chemistry and Physics, 16, 1029–1043, doi:10.5194/acp-16-1029-2016, 2016.

Olsen, J., Anderson, N. J., and Knudsen, M. F.: Variability of the North Atlantic Oscillation over the past 5,200 years, Nature Geoscience, 5, 808–812, 2012.

Oros, D. R. and Simoneit, B. R. T.: Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 1. Temperate climate conifers, Applied Geochemistry, 16, 1513–1544, doi:10.1016/s0883-2927(01)00021-x, 2001a.

Oros, D. R. and Simoneit, B. R. T.: Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 2. Deciduous trees, Applied Geochemistry, 16, 1545–1565, doi:10.1016/S0883-2927(01)00022-1, 2001b.

Oros, D. R., Abas, M. R. b., Omar, N. Y. M. J., Rahman, N. A., and Simoneit, B. R. T.: Identification and emission factors of molecular tracers in organic aerosols from biomass burning: Part 3. Grasses, Applied Geochemistry, 21, 919–940, doi:10.1016/j.apgeochem.2006.01.008, 2006.

PAGES 2k Consortium, .: Continental-scale temperature variability during the past two millennia, Nature Geoscience, 6, 339–346, doi:10.1038/ngeo1797, 2013.

Pohjola, V. A., Moore, J. C., Isaksson, E., Jauhiainen, T., van de Wal, R. S. W., Martma, T., Meijer, H. A. J., and Vaikmäe, R.: Effect of periodic melting on geochemical and isotopic signals in an ice core from Lomonosovfonna, Svalbard, Journal of Geophysical Research: Atmospheres, 107, ACL 1–1–ACL 1–14, doi:10.1029/2000JD000149, 2002.

Power, M., Marlon, J., Ortiz, N., Bartlein, P., Harrison, S., Mayle, F., Ballouche, A., Bradshaw, R., Carcaillet, C., Cordova, C., Mooney, S., Moreno, P., Prentice, I., Thonicke, K., Tinner, W., Whitlock, C., Zhang, Y., Zhao, Y., Ali, A., Anderson, R., Beer, R., Behling, H., Briles, C., Brown, K., Brunelle, A., Bush, M., Camill, P., Chu, G., Clark, J., Colombaroli, D., Connor, S., Daniau, A. L., Daniels, M., Dodson, J., Doughty, E., Edwards, M., Finsinger, W., Foster, D., Frechette, J., Gaillard, M. J., Gavin, D., Gobet, E., Haberle, S., Hallett, D., Higuera, P., Hope, G., Horn, S., Inoue, J., Kaltenrieder, P., Kennedy, L., Kong, Z., Larsen, C., Long, C., Lynch, J., Lynch, E., McGlone, M., Meeks, S., Mensing, S., Meyer, G., Minckley, T., Mohr, J., Nelson, D., New, J., Newnham, R., Noti, R., Oswald, W., Pierce, J., Richard, P., Rowe, C., Sanchez Goñi, M., Shuman, B., Takahara, H., Toney, J., Turney, C., Urrego-Sanchez, D., Umbanhowar, C., Vandergoes, M., Vanniere, B., Vescovi, E., Walsh, M., Wang, X., Williams, N., Wilmshurst, J., and Zhang, J.: Changes in fire regimes since the Last Glacial Maximum: an assessment based on a global synthesis and analysis of charcoal data, Climate Dynamics, 30, 887–907, doi:10.1007/s00382-007-0334-x, 2008.

Power, M., Mayle, F., Bartlein, P., Marlon, J., Anderson, R., Behling, H., Brown, K., Carcaillet, C., Colombaroli, D., Gavin, D., Hallett, D., Horn, S., Kennedy, L., Lane, C., Long, C., Moreno, P., Paitre, C., Robinson, G., Taylor, Z., and Walsh, M.: Climatic control of the biomass-burning decline in the Americas after AD 1500, The Holocene, 23, 3–13, doi:10.1177/0959683612450196, 2013.

Randerson, J. T., Liu, H., Flanner, M. G., Chambers, S. D., Jin, Y., Hess, P. G., Pfister, G., Mack, M. C., Treseder, K. K., Welp, L. R., Chapin, F. S., Harden, J. W., Goulden, M. L., Lyons, E., Neff, J. C., Schuur, E. A. G., and Zender, C. S.: The Impact of Boreal Forest Fire on Climate Warming, Science, 314, 1130–1132, 10.1126/science.1132075, 2006.

Rubino, M., D'Onofrio, A., Seki, O., and Bendle, J. A.: Ice-core records of biomass burning, The Anthropocene Review, 3, 140–162, doi:10.1177/2053019615605117, 2016.

Ruesch, A. and Gibbs, H. K.: New IPCC Tier-1 global biomass carbon map for the year 2000, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, 2008.

Savarino, J. and Legrand, M.: High northern latitude forest fires and vegetation emissions over the last millennium inferred from the chemistry of a central Greenland ice core, Journal of Geophysical Research: Atmospheres, 103, 8267–8279, doi:10.1029/97JD03748, 1998.

Simoneit, B., Schauer, J., Nolte, C., Oros, D., Elias, V., Fraser, M., Rogge, W., and Cass, G.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, Atmospheric Environment, 33, 173–182, doi:10.1016/S1352-2310(98)00145-9, 1999.

Simoneit, B. R. and Elias, V. O.: Organic tracers from biomass burning in atmospheric particulate matter over the ocean, Marine Chemistry, 69, 301–312, doi:10.1016/S0304-4203(00)00008-6, 2000.

Simoneit, B. R. T.: Biomass burning - A review of organic tracers for smoke from incomplete combustion, Applied Geochemistry, 17, 129–162, doi:10.1016/S0883-2927(01)00061-0, 2002.

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

Slade, J. H. and Knopf, D. A.: Heterogeneous OH oxidation of biomass burning organic aerosol surrogate compounds: assessment of volatilisation products and the role of OH concentration on the reactive uptake kinetics., Physical Chemistry Chemical Physics, 15, 5898–915, doi:10.1039/C3CP44695F, 2013.

Soja, A. J., Tchebakova, N. M., French, N. H., Flannigan, M. D., Shugart, H. H., Stocks, B. J., Sukhinin, A. I., Parfenova, E., III, F. S. C., and Jr., P. W. S.: Climate-induced boreal forest change: Predictions versus current observations, Global and Planetary Change, 56, 274 – 296, doi:http://dx.doi.org/10.1016/j.gloplacha.2006.07.028, 2007.

Stein, A., Draxler, R., Rolph, G., Stunder, B., Cohen, M., and Ngan, F.: NOAA's HYSPLIT atmospheric transport and dispersion modeling system, Bulletin of the American Meteorological Society, 96, 2059–2077, doi:10.1175/BAMS-D-14-00110.1, 2015.

Stohl, A., Berg, T., Burkhart, J., Fjæraa, A., Forster, C., Herber, A., Hov, Ø., Lunder, C., McMillan, W., Oltmans, S., Shiobara, M., Simpson, D., Solberg, S., Stebel, K., Ström, J., Tørseth, K., Treffeisen, R., Virkkunen, K., and Yttri, K. E.: Arctic smoke–record high air pollution levels in the European Arctic due to agricultural fires in Eastern Europe in spring 2006, Atmospheric Chemistry and Physics, 7, 511–534, doi:10.5194/acp-7-511-2007, 2007.

Thompson, L. G., Davis, M. E., Mosley-Thompson, E., Sowers, T. A., Henderson, K. A., Zagorodnov, V. S., Lin, P.-N., Mikhalenko, V. N., Campen, R. K., Bolzan, J. F., Cole-Dai, J., and Francou, B.: A 25,000-Year Tropical Climate History from Bolivian Ice Cores, Science, 282, 1858–1864, doi:10.1126/science.282.5395.1858, 1998.

Torrence, C. and Compo, G. P.: A practical guide to wavelet analysis, Bulletin of the American Meteorological society, 79, 61–78, doi:10.1175/1520-0477(1998)079<0061:APGTWA>2.0.CO;2, 1998.

Trouet, V., Esper, J., Graham, N. E., Baker, A., Scourse, J. D., and Frank, D. C.: Persistent Positive North Atlantic Oscillation Mode Dominated the Medieval Climate Anomaly, Science, 324, 78–80, doi:10.1126/science.1166349, 2009.

Trouet, V., Scourse, J., and Raible, C.: North Atlantic storminess and Atlantic Meridional Overturning Circulation during the last Millennium: Reconciling contradictory proxy records of NAO variability, Global and Planetary Change, 84–85, 48–55, doi:10.1016/j.gloplacha.2011.10.003, 2012.

van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009), Atmospheric Chemistry and Physics, 10, 11 707–11 735, doi:10.5194/acp-10-11707-2010, 2010.

Wang, Y., Cheng, H., Edwards, R. L., He, Y., Kong, X., An, Z., Wu, J., Kelly, M. J., Dykoski, C. A., and Li, X.: The Holocene Asian Monsoon: Links to Solar Changes and North Atlantic Climate, Science, 308, 854–857, doi:10.1126/science.1106296, 2005.

Wang, Z., Chappellaz, J., Park, K., and Mak, J.: Large variations in Southern Hemisphere biomass burning during the last 650 years, Science, 330, 1663–1666, doi:10.1126/science.1197257, 2010.

Wendl, I., Eichler, A., Isaksson, E., Martma, T., and Schwikowski, M.: 800-year ice-core record of nitrogen deposition in Svalbard linked to ocean productivity and biogenic emissions, Atmospheric Chemistry and Physics, 15, 7287–7300, doi:10.5194/acp-15-7287-2015, 2015.

Wessel, P. and Smith, W. H.: A global, self-consistent, hierarchical, high-resolution shoreline database, Journal of Geophysical Research: Solid Earth, 101, 8741–8743, doi:10.1029/96JB00104, 1996.

Zagorodnow, V. S.: Recent Soviet activities on ice core drilling and core investigations in Arctic region, Bull. Glacier Res., p. 81–84, 1988.

Zangrando, R., Barbaro, E., Zennaro, P., Rossi, S., Kehrwald, N. M., Gabrieli, J., Barbante, C., and Gambaro, A.: Molecular markers of biomass burning in Arctic aerosols, Environmental science & technology, 47, 8565–8574, doi:10.1021/es400125r, 2013.

Zangrando, R., Barbaro, E., Vecchiato, M., Kehrwald, N. M., Barbante, C., and Gambaro, A.: Levoglucosan and phenols in Antarctic marine, coastal and plateau aerosols, Science of The Total Environment, 544, 606 – 616, doi:10.1016/j.scitotenv.2015.11.166, 2016.

Zennaro, P., Kehrwald, N., McConnell, J. R., Schüpbach, S., Maselli, O. J., Marlon, J., Vallelonga, P., Leuenberger, D., Zangrando, R., Spolaor, A., Borrotti, M., Barbaro, E., Gambaro, A., and Barbante, C.: Fire in ice: two millennia of boreal forest fire history from the Greenland NEEM ice core, Climate of the Past, 10, 1905–1924, doi:10.5194/cp-10-1905-2014, 2014.

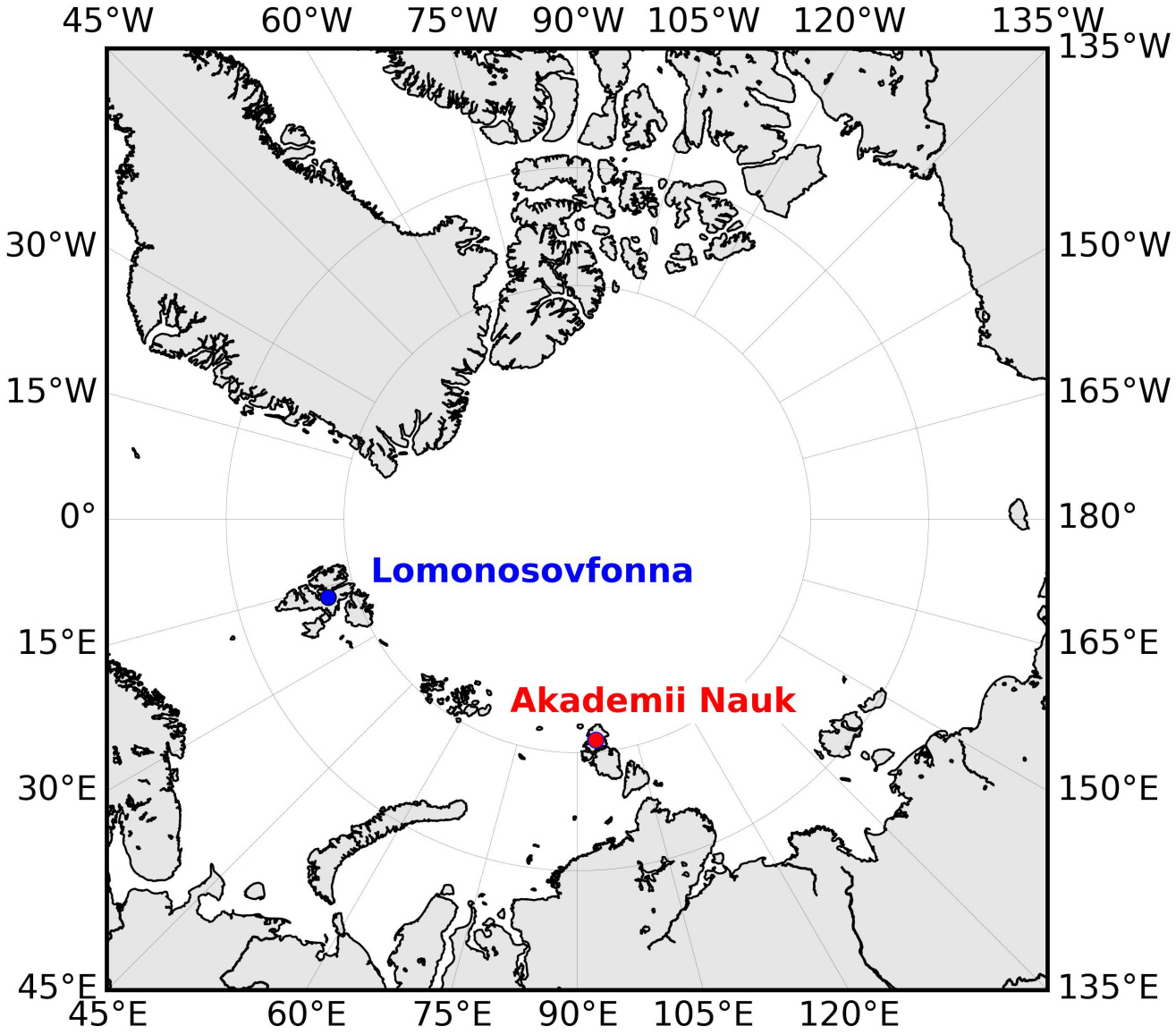


Figure 1. Location of Lomonosovfonna ice core drilling site on the island of Spitsbergen in Svalbard (78°49'24.4"N, 17°25'59.2"E) and the Akademii Nauk ice core drilling site on Severnaya Zemlya (80°31'N, 94°49'E). The map was produced in the Python "matplotlib" graphics environment (Hunter, 2007).

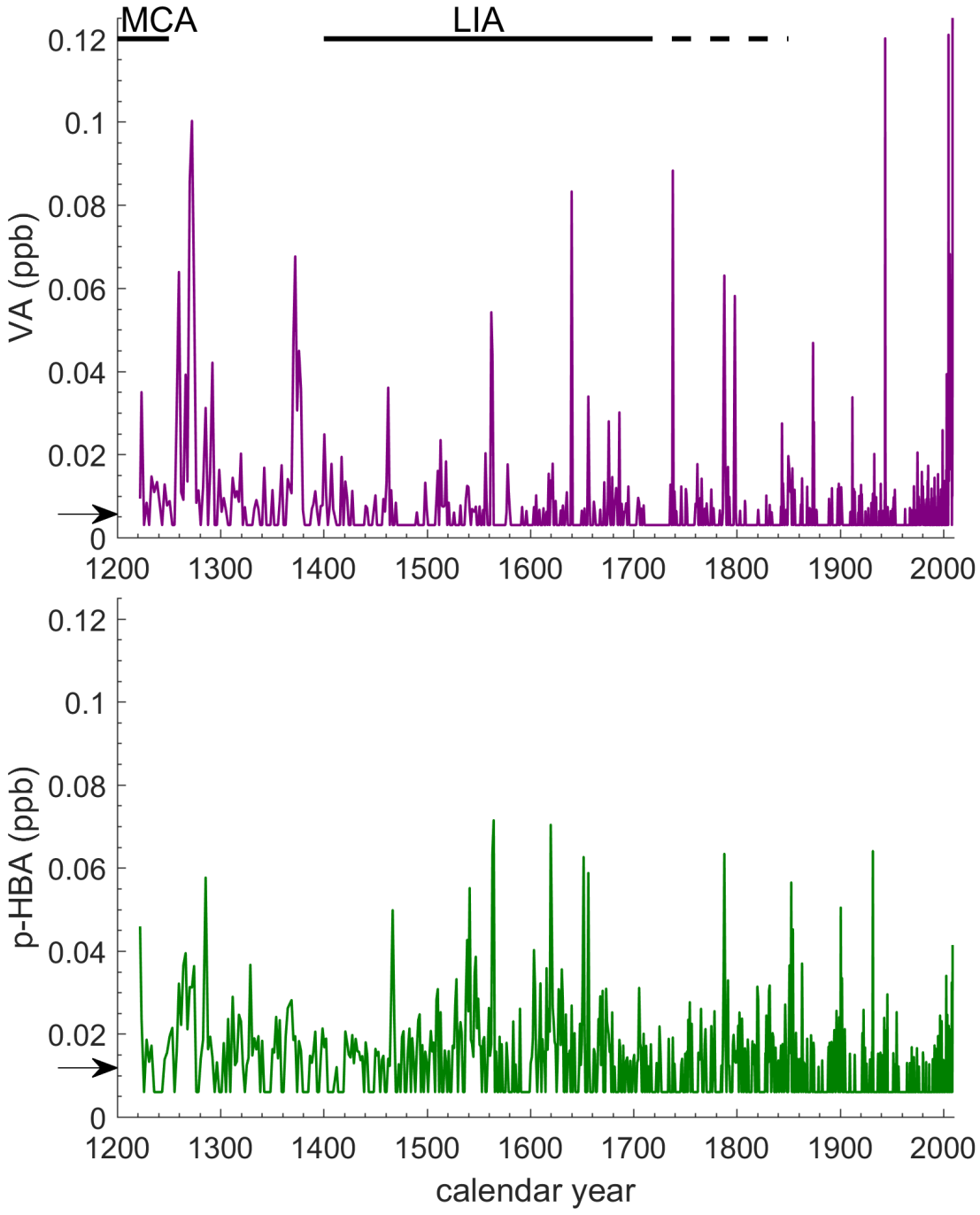


Figure 2. Aromatic acids in the Lomonosovfonna, Svalbard ice core. Top: vanillic acid, Bottom: p-hydroxybenzoic acid. Arrows are the detection limits. The black horizontal lines are the Medieval Climate Anomaly (MCA) and the Little Ice Age (LIA) (Mann et al., 2009). The dashed horizontal line is the extended LIA in the Svalbard region (Divine et al., 2011).

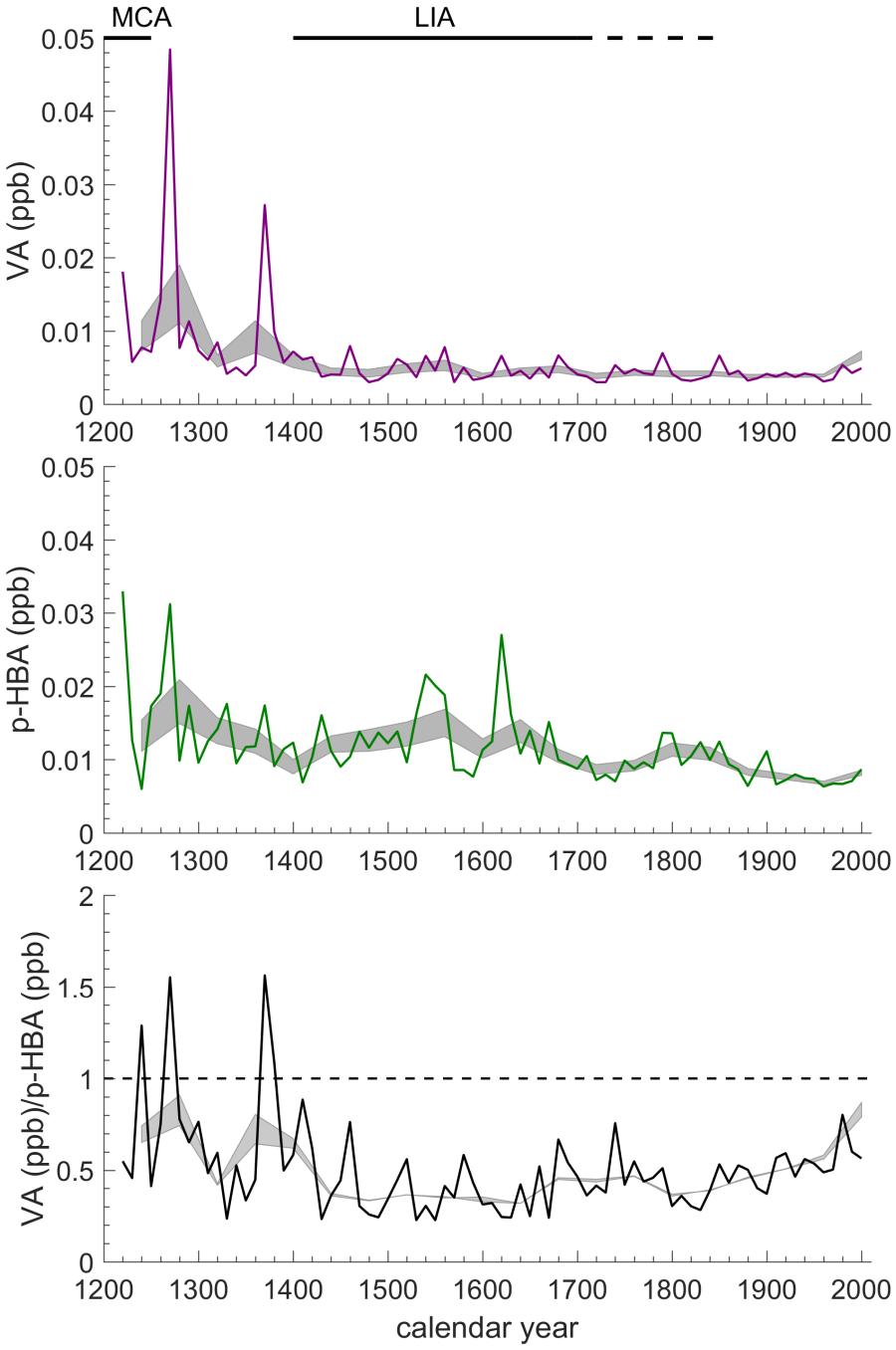


Figure 3. Lomonosovfonna ice core records of vanillic acid (top) and p-hydroxybenzoic acid (middle) and the ratio of vanillic acid/p-hydroxybenzoic acid (bottom). For all plots: ~~black~~ solid lines are 10-year bin averages, gray shaded areas are 40-year bin averages of ±1 standard error. The dashed line on the bottom plot indicates a ratio of 1. The black horizontal lines are the Medieval Climate Anomaly (MCA) and the Little Ice Age (LIA) (Mann et al., 2009). The dashed horizontal line at the top is the extended LIA in the Svalbard region (Divine et al., 2011).

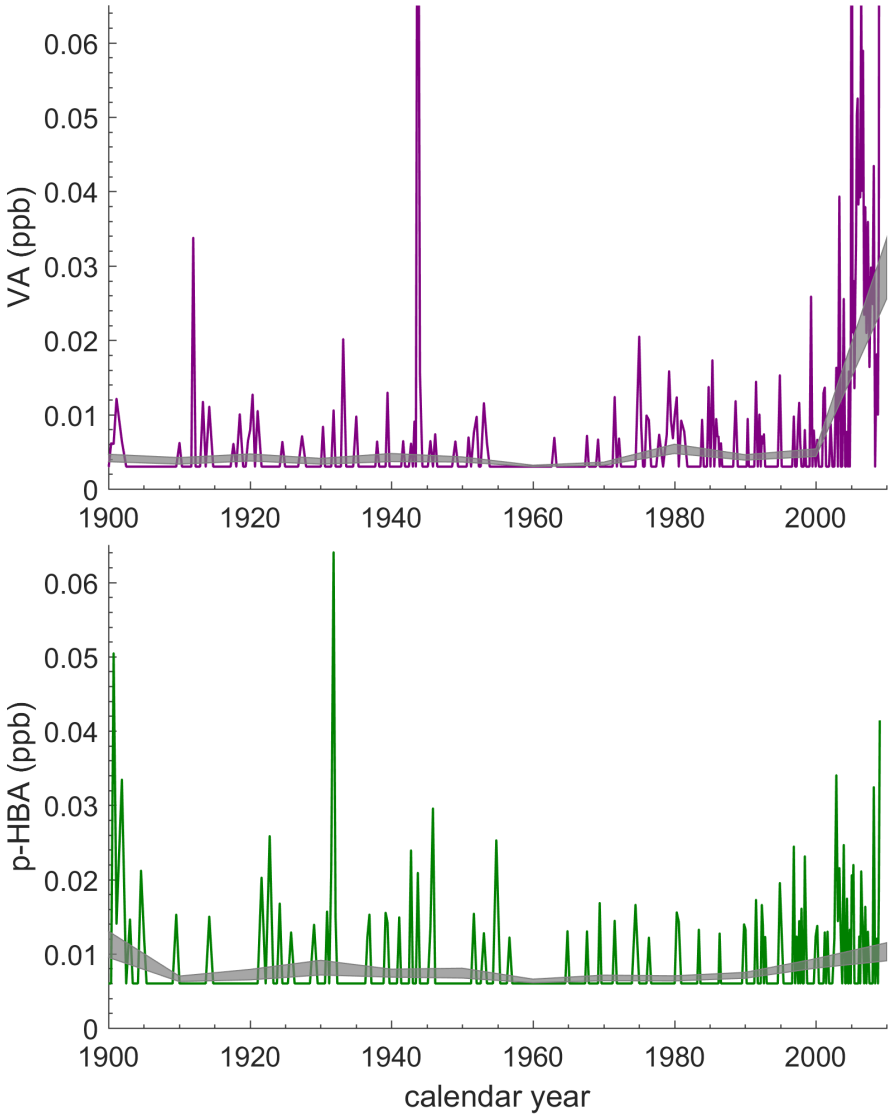


Figure 4. Lomonosovfonna ice core records of vanillic acid (top) and p-hydroxybenzoic acid (bottom) for the 20th century. Gray shaded areas are 10-year bin averages with ±±1 standard error.

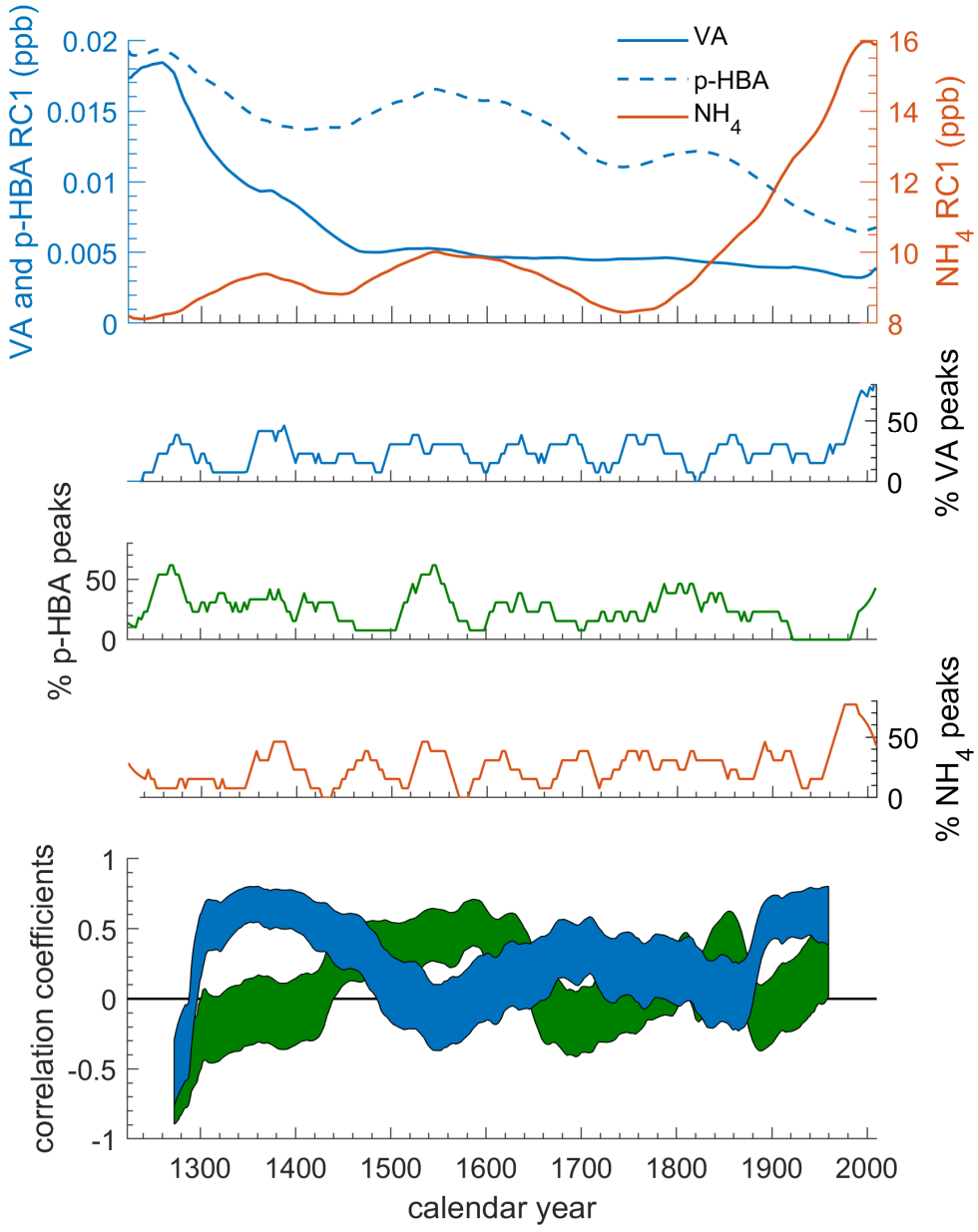


Figure 5. Relationships between Lomonosovfonna vanillic acid (VA), p-hydroxybenzoic acid (p-HBA), and ammonium (NH_4) using 3-year bin averaged data. 1) First component from the singular spectrum analysis of VA (blue solid line), p-HBA (blue dashed line), and NH_4 (orange line) (PC1) reconconstructed into concentration units (RC1, ppb), 2-4) Frequency of peaks in the ice core signals reconstructed using singular spectrum components 2-30 and peak threshold of 75th percentile, smoothed with a 40-year running window. 5) Correlation coefficients for the ice core peak frequencies using a 200-year running window ($p<0.001$). Bands are the 95% confidence intervals of the correlation coefficients of VA and ammonium (blue) and p-HBA and ammonium (green).

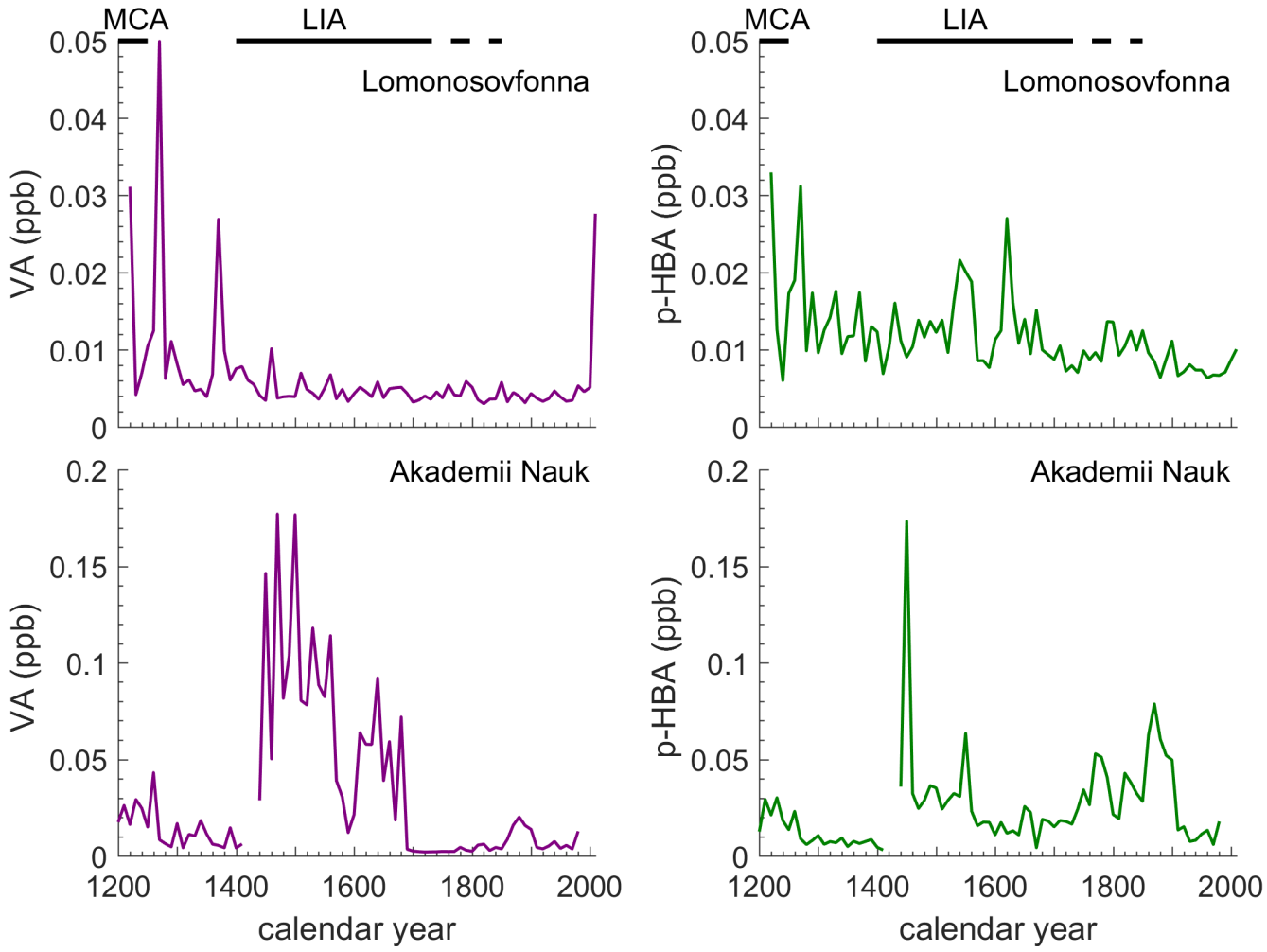


Figure 6. Aromatic acids in the Lomonosovfonna, Svalbard and Akademii Nauk ice cores. Left: vanillic acid, Right: p-hydroxybenzoic acid. ~~Black~~ Violet lines are 10-year bin averages of the the Lomonosovfonna ice core measurements. ~~Grey~~ Green lines are the 10-year bin averages of the Akademii Nauk ice core measurements (Grieman et al., 2017). The black horizontal lines are the Medieval Climate Anomaly (MCA) and the Little Ice Age (LIA) (Mann et al., 2009). The dashed horizontal line is the extended LIA in the Svalbard region (Divine et al., 2011).

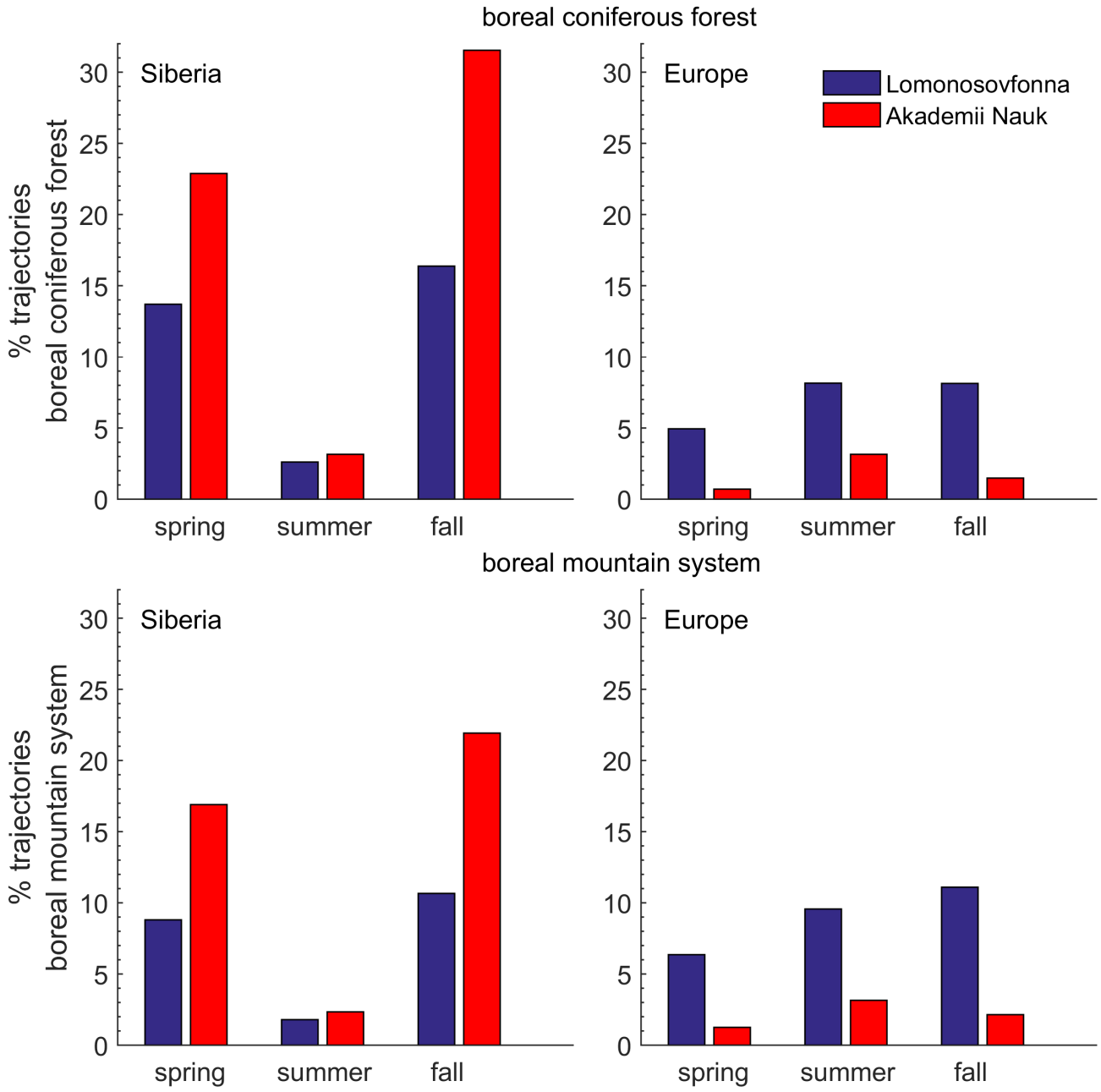


Figure 7. ~~Back~~ 10-day back trajectories from 2006-2015 reaching the boreal ecosystems starting from the Lomonosovfonna and Akademii Nauk ice core locations. Blue is Lomonosovfonna. Red is Akademii Nauk. Trajectories reaching: Siberia (left), Europe (right), boreal coniferous forest (top), and boreal mountain system (bottom).

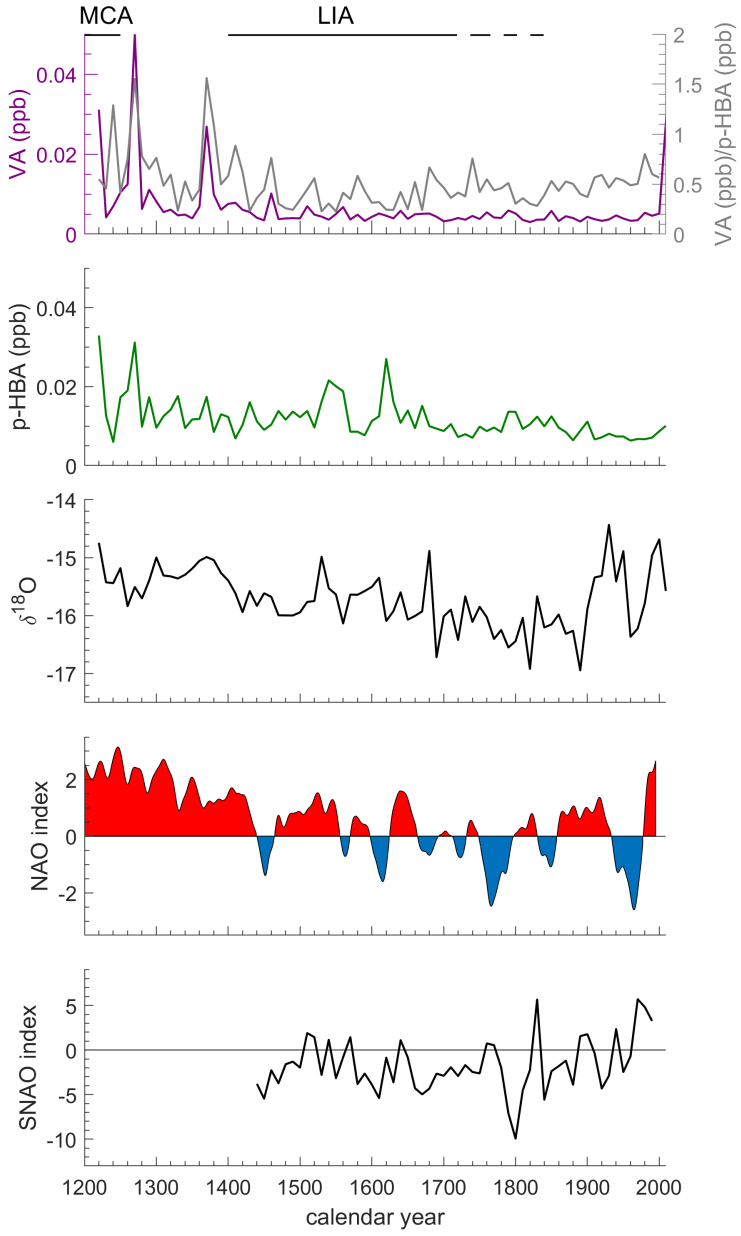
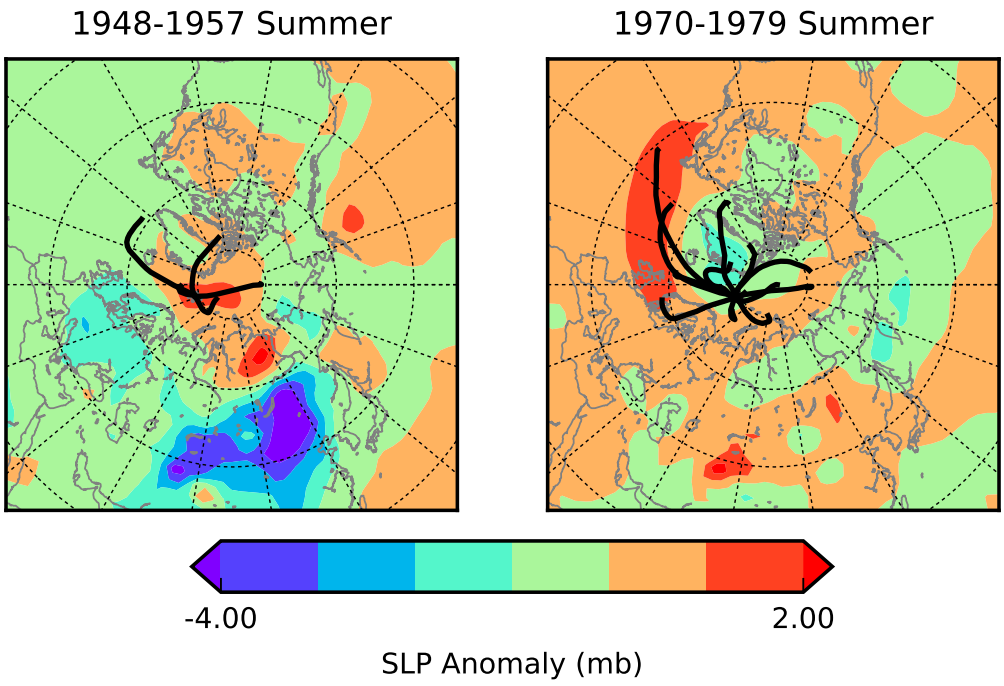


Figure 8. Comparison of the timing of aromatic acid signals in the Lomonosovfonna ice core over the past 800 years compared to other climate-related proxy records. From top: 10-year bin averages of Lomonosovfonna vanillic acid (violet line), ratio of vanillic acid/p-hydroxybenzoic acid (gray line), and p-hydroxybenxoic acid; 10-year bin averages of the oxygen isotope record from the Lomonosovfonna ice core (Wendl et al., 2015); ~~10-year bin averages of the GISP2 ice core D seasalt sodium (lower values correspond to positive NAO; Mayewski et al., 1997);~~ North Atlantic Oscillation (NAO) index (red > 0; blue < 0; Trouet et al., 2009); ~~NAO index (Olsen et al., 2012) (red > 0; blue < 0);~~ and 10-year bin averages of the summer North Atlantic Oscillation (SNAO) index (Linderholm et al., 2009). The black horizontal lines are the timing of the Medieval Climate Anomaly (MCA) and the Little Ice Age (LIA) (Mann et al., 2009). The dashed horizontal line is the extended LIA in the Svalbard region (Divine et al., 2011).

~~Back trajectories reaching the boreal ecosystems starting from the Lomonosovfonna ice core location. Blue is a positive SNAO period (1970-1979 CE). Red is a negative SNAO period (1948-1957 CE). Trajectories reaching: Siberia (left), Europe (right), boreal coniferous forest (top), and boreal mountain system~~



~~(bottom).~~

Figure 9. 10-day clustered back trajectories starting from the Lomonosovfonna ice core location superimposed on sea level pressure anomalies for summer (June-August) of 1948-1957 (negative SNAO) and 1970-1979 (positive SNAO). Anomalies are relative to the 1948-2017 mean of NCEP/NCAR reanalysis data.