 # Reviewer *2*

"Ice core records of biomass burning tracers (levoglucosan, dehydroabietic and vanillic acids) from Aurora Peak in Alaska since 1660s: A new dimension of forest fire activities in the Northern Hemisphere" by Ambarish Pokhrel and co-workers.

Overall evaluation:

The topics is of importance since fires are a major source of gases and aerosols that strongly impact chemical composition of the atmosphere and the radiation balance. In turn, climate changes directly disturb the fire regime, for instance through the duration of fire weather conditions and changes in vegetation, particularly in the boreal regions. In addition to this overall interest, the data presented in this paper would be useful to discuss the consistency between these three organic markers (levoglucosan, dehydroabietic and vanillic acids) and other potential proxy including ammonium. However, as it stands, the paper suffers from too many weaknesses to be recommended for publication at the ACP journal. I recommend to the authors to take time to revisit the existing literature and their data.
Major weaknesses:

1. Quality of the Aurora ice record: Some key information are missed in the manuscript for the reader to evaluate the quality Aurora ice core record. Indeed, when using an ice core record to infer atmospheric information, the reader (and the reviewers) needs to have some basic information that are not given in section 2 (Materials and Methods). I think that, given the rather low elevation (2850 m) of the Aurora site, we may expect frequent melting. If, so that has to be clearly stated in the manuscript and the authors would discuss the possible consequence for the quality of the ice record in terms of atmospheric signal. Since the effect of melting is not well know for organics, it would be nice to show the record of major ions (including ammonium, nitrate, and sulfate). Checking your Figure 4, i am very surprised by the nitrate levels that are shown to range between 0 and 34 ppb (i.e., very low levels). At the opposite, the nss-K level (ranging from 0 to around 50 ppb) exhibits several values exceeding 15 ppb (which is a lot): how much abundant is calcium in this core? (see my further comments on the use of fine potassium).

Responsse: Thank you very much.

The annual snow accumulation rate is 8 mm yr^{-1} since 1900 to onwards and drastically accumulated at a rate of 23 mm yr^{-1} after the Great Pacific Climate Shift. Meanwhile, the average temperature anomalies for 1923-1942, 1943-1945, and 1976-2007 were +0.73, -0.65 and +0.55°C, respectively (Tsushima et al., 2015).

We assumed that there was not 100 percent melting of snowfall in the saddle of the Aurora. The correlations of δD record of this ice core and detrended annual accumulation rates of snowfall are well correlated with air temperature and precipitation amount of Aurora.

The average annual amplitude of δD from this ice core is 30.9%. This high amplitude (more than 30%) cannot be maintained, if there was intensive melting (100%) in the past (Tsushima et al., 2015). Please see lines 536-545.

We are preparing a separate manuscript of ions. We are very sorry to say that we would like to remove Fig. 4 and explanation of this figure. Hence, this time we have deleted these two paragraphs and Fig.4.

2. Inconsistencies: Since you will discuss in section 3 (as also mentioned in the abstract) the correlations of levoglucosan with NO2-, NO3-, nss-SO42-, nss-K+, and NH4+ that are all insignificant (suggesting that these anions and cations do not represent a gleaming signal of biomass burning activities in the source regions for southern Alaska)), it would be nice to show the profiles. This need to report these profiles also comes from the fact this observed absence of correlations contrasts with the statement that I find in the paper from Tsushima et al. (2005) stating "To confirm the dating based on D and Na+ seasonal cycles, we compared the dating of the ice core with reference horizons of known age (Fig. 3). We found a large peak of NO3 and NH4+ and a visible dirty layer at 8.55 m w.eq., which we ascribed to the year 2004. Generally, NO3 and NH4+ are released by forest fires (e.g., Legrand and Mayewski, 1997; Eichler et al., 2011). » This point clearly needs to be discussed showing all the records, i think. Since, as also suggested by your figure 5, the 2004 year was characterized by large fires in Alaska, please also comment your organic records for this year ?
Response: Thank you very much. This time we have removed that ionic part in the revised MS. We are preparing another paper for ions.

We did not obtain high value of levoglucosan (95.3 ng/kg-ice) compared to its average (543). But dehydroabietic (309.7) and vanillic (2.70) acids showed higher concentrations compared to their average (62 and 1.6 ng/kg-ice, respectively). Hence, there is more local influence for dehydroabeitic and vanillic acids.
Please also see Figure 6e in the revised MS.

3. Numerous previous works are not cited or adequately cited in the manuscript: In the introduction and at several places in the text, the previous works done on fire records in ice cores are not adequately cited, and some important references are missed including two reviews papers (see the list below). For example, you extensively cited the paper from Whitlow et al. (1994) for ammonium and nitrate biomass burning events that just follows the pioneering study from Legrand et al. (1992) for ammonium, nitrate and carboxylates. After the publication of these two papers, it becomes clear that, although some ammonium spikes are sometimes accompanied by nitrate peaks, it is not a general rule (Savarino and Legrand, 1998). This point was extensively discussed in the review from Legrand et al. (2016). The same is true for the non-sea-salt and non-dust potassium fraction. On this topic, in your manuscript I would recommend to report nss-non-dust-potassium (calculated by using your calcium data).
Finally, none of the Greenland ice core studies reported a sulfate perturbation with biomass burning peaks. So I will be more careful about that at line 246.
Response: Thank you very much. By taking the reviewer's comment, we have cited all these research papers in the revised MS.

We are preparing another paper by focusing on ions. Nss-non-dust K^+ calculation is of great interest. We will certainly report nss-non-dust K fraction in another paper. Hence, we have decided to delete all the ionic parts from this MS.

Legrand M., M. De Angelis, T. Staffelbach, A. Neftel, and B. Stauffer, Large perturbations of ammonium and organic acids content in the Summit Greenland ice core, fingerprint from forest fires ?, Geophys. Res. Lett., 19, 473-475, 1992.
Legrand M., and M. De Angelis, Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone, J. Geophys. Res., 101, 4129-4145, 1996.
Savarino, J., and M. Legrand, High northern latitude forest fires and vegetation emissions over the last millenium inferred from the chemistry of a central Greenland ice core, J. Geophys. Res., 103, 8267-8279, 1998.
Legrand, M., McConnell, J., Fischer, H., Wolff, E. W., Preunkert, S., Arienzo, M., Chellman, N., Leuenberger, D., Maselli, D., Place, P., Sigl, M., Schüpbach, S., and Flannigan, M.: Boreal fire records in Northern Hemisphere ice cores: A review, Clim. Past, 12, 2033-2059, doi:10.5194/cp-12-2033-2016, 2016.
Rubino, M., D'Onofrio, A., Seki, O., and Bendle, J.A., Ice-core records of biomass burning, The Anthropocene Review, vol. 3(2), 140-162, DOI: 10.1177/2053019615605117, 2016.
Grieman, M. M., Aydin, M., Isaksson, E., Schwikowski, M., and Saltzman, E. S.:Aromatic acids in an Arctic ice core from Svalbard: a proxy record of biomass burning, Clim. Past, 14, 637-651, https://doi.org/10.5194/cp-14-637-2018, 2018.

4. The wording is sometimes too vague or unclear, figures are unclear: I don't understand the meaning of "A new dimension of forest fire activities in the Northern Hemisphere" in the title.
Response: Thank you, we have changed the title. Please see lines 1-4 in the revised MS.

Line 29: what do you mean with "different ice core studies": Please specify from where ?, with which proxy ?, which time period ?
Response: Thank you for the question. We have improved this line and mentioned clearly Kamchatka (Kawamura et al., 2012), Mt. Logan (Robock et al., 1991), Svalbard, Akademii Nauk and Tunu (Grieman et al., 2018a,b; 2017), and Greenland (Whitlow et al., 1994) ice core studies in the revised MS. Please see Figures 6 (a-e). Please see lines 34-36.

Lines 236 and 239: what are these numbers: concentrations of ammonium ? of levoglucosan ? Why figure 3 reports levoglucosan only up to 600 ng L-1 and Figure 4 only up to 1200 ng L-1 while Figure 2 indicates levo as high as 20802 ng L-1 ?
Please show satellite data for Siberia as well in Figure 5.
Response: Thank you. Figure 3 is the correlation analysis for the period of 1977-2007 (i.e., after the Great Pacific Climate Shift). Concentrations of these compounds are within 600 ng/kg-ice. We can see in the figure caption too. We have prepared air mas backward trajectories (500 hPa) in the revised MS. Please Figure 7a-f. Please see lines 160-173.

5. Information derived from Back-ward trajectories: I think you may address more details on the origin of air mass reaching the Aurora site. In the present manuscript you stated at the end of the introduction: "Particularly, 10 day backward trajectory from 1992-2002

showed that southern Alaska can receive air masses from the North Pacific Regions, East Asia, Eastern Russia-Siberia, higher latitudes of Alaskan regions, Japan, and Canadian regions in the troposphere (>300 hPa) (Yasunari and Yamazaki, 2009)."
I here recommend to address the following points (that would need new calculations): (1) focus on the fire season (from June to August), (2) I think 300 hPa is too high (it is the upper troposphere) and 500 hPa (around 5 km elevation) is likely more relevant for the travel of plumes. Also check the sensitivity between 5 and 10 days.
Response: Thank you. By taking reviewer comments, we have added Air mass Backward trajectories (500 hPa) with fire counts for whole year. Please see Figure 7a-f.

6. Discussion with previous records (section 3.4): Why do you extensively discuss your organics with ammonium records from 20D (Greenland) ? This discussion is not very useful since the records were obtained with different proxy and are expected to be influenced by different source regions (Canada for Greenland versus Alaska and may be Siberia for Aurora). Instead, again please show your own (Aurora) data on ammonium, nitrate, potassium, sulfate etc.
Response: Thank you. We have deleted ionic parts from this section of 3.4 (i.e., comparison with ammonium, nitrite, nitrate and sulphate of same ice core) as mentioned above.

This time, we compared this study with other ice core studies of biomass burning tracers in the section 3.4 (i.e., Biomass burning tracers, Temperature, and Climate variability: Atmospheric consequences) in the revised MS. Please see section 3.4.

Reviewers #3

Interactive comment on "Ice core records of biomass burning tracers (levoglucosan, dehydroabietic and vanillic acids) from Aurora Peak in Alaska since 1660s: A new dimension of forest fire activities in the Northern Hemisphere" by Ambarish Pokhrel et al.

Received and published: 10 April 2019

This manuscript presents records of the biomass burning tracers levoglucosan, dehydroabietic acid and vanillic acid from an ice core retrieved at Aurora Peak, Alaska, and covering the time period from ca. 1660 to 2009. In general, this seems to be a high quality data set, which may be interesting and may deserve publication, since only few ice core records of such tracers are available up to now. Unfortunately, the manuscript does not meet basic scientific criteria, as outlined below, is very descriptive and not well-written (requires English editing), and lacks a clear structure, which makes it hard to digest. Before becoming publishable, major revisions are therefore required.

1. Method description is incomplete (no detection limits) and basic ice core data are missing (dating, dating uncertainty, melt extend, etc.).
   Response: Thank you. Taking reviewer comment, we have added several paragraphs on methods in this section 2. Please see revised section 2.

2. The record presented is incomplete, only 40% of the core was analysed, i.e. the records are not suitable to discuss short-term biomass burning events.
   Response: Thank you very much. Only 40% samples were available for analyzing organic compounds (e.g., anhydrosugars). Based upon the available data, we have discussed the source of biomass burning tracers as best as we could.

3. Records should not be shown as continuous line; data points should indicate for which time period they are representative.
   Response: Thank you. We have added new figure in the revised MS. Please see Figure 2.

4. The Aurora ice core is affected by melting with melt feature percentages of up to 100%. It should be discussed how this effects the records of biomass burning tracers.
   Response: Thank you very much.
   The annual snow accumulations rate is 8 mm yr^{-1} since 1900 to onwards and drastically increase to 23 mm yr^{-1} after the Great Pacific Climate Shift. Meanwhile, the average temperature anomalies for 1923-1942, 1943-1945, and 1976-2007 were +0.73, -0.65 and +0.55°C, respectively (Tsushima et al., 2015). Please see line 536.

   We assumed that there was not 100 percent melting of snowfall in the saddle of the Aurora. The correlations of δD record of this ice core and detrended annual accumulation rates of snowfall are well correlated with air temperature and precipitation amount at Aurora. The average annual amplitude of δD from this ice core is 30.9%. This high amplitude of 30% cannot be maintained if a higher percentage (e.g., 100%) of the melting occurred in the past (Tsushima et al., 2015; Tsushima, 2015). These points are added in the revised MS.

Please see lines 113-116 and 536-545.

5. Recent other publications in this field should be discussed and cited (list at the end of this review).
   Response: Thank you. We have used new potential papers throughout the MS. Please see revised MS.

6. There is no discussion with respect to other available data. Concentrations in the Aurora core seem to be higher than in the Kamchatka core, although Aurora is located much further away from the sources.
   Response: We compared our data with several other ice core studies in the revised MS. Please see Figure 6a-e.

7. What is the reasoning behind conducting a correlation analysis with nss-sulphate and nss-calcium. They are not expected to have a biomass burning source. Where the ion records averaged to match the incomplete sampling of the organic tracers?
   Response: Thank you. We have deleted these paragraphs.

8. It is unclear what can be learned from the fire spot data. Here you need to come up with a quantitative number to compare with ice core records.
   Response: We have prepared new fire counts with fire intensity and air mass backward trajectories. Please see Figure 7(a-f).

9. There are no conclusions, just a summary.
   Response: Thank you, this time we have added new paragraphs in this section. Please see the summary and conclusions in the revised MS.

10. Fig. 1: Already shown in Pokhrel et al., 2015 and Pokhrel et al., 2016, is this not a copyright issue?
    Response: Thank you. We have changed it. Please see Figure 1.

Thank you very much for your valuable time and comments.

Gambaro, A., et al. (2008). "Direct Determination of Levoglucosan at the Picogram per Milliliter Level in Antarctic Ice by High-Performance Liquid Chromatography/Electrospray Ionization Triple Quadrupole Mass Spectrometry." Analytical Chemistry 80(5): 1649-1655.
Grieman, M. M., et al. (2017). "Aromatic acids in a Eurasian Arctic ice core: a 2600- year proxy record of biomass burning." Clim. Past 13(4): 395-410. Grieman, M. M., et al. (2018). "Aromatic acids in an Arctic ice core from Svalbard: a proxy record of biomass burning." Clim. Past 14(5): 637-651.
Grieman, M. M., et al. (2018) "Burning-derived vanillic acid in an Arctic ice core from Tunu, northeastern Greenland." Clim. Past 14(11): 1625-1637.
Grieman, M. M., et al. (2015). "A method for analysis of vanillic acid in polar ice cores." Clim. Past 11(2): 227-232.
Kehrwald, N., et al. (2012). "Levoglucosan as a specific marker of fire events in Greenland snow." Tellus B: Chemical and Physical Meteorology 64(1): 18196.
Zennaro, P., et al. (2014). "Fire in ice: two millennia of boreal forest fire history from the Greenland NEEM ice core." Clim. Past 10(5): 1905-1924.

Responses to reviewers' comments (responses are in blue)

Anonymous Referee (*ACP 2019-139*) #1

Interactive comment on "Ice core records of biomass burning tracers (levoglucosan, dehydroabietic and vanillic acids) from Aurora Peak in Alaska since 1660s: A new dimension of forest fire activities in the Northern Hemisphere" by Ambarish Pokhrel et al. Received and published: 27 March 2019.

GENERAL COMMENTS: The authors present a record of three biomass burning tracers (levoglucosan, dehydroabietic and vanillic acids) from the Aurora Peak ice core from southern Alaska. The North Pacific contains few long fire records, and this study adds a valuable location for a biomass burning record. I commend the authors for determining multiple fire tracers within the same ice core and for investigating the different types of information that can be gained from each marker. The authors compare their results with the Kamchatka ice core as well as multiple Greenland ice cores. The comparison with Kamchatka is much more applicable, as these cores are both within the North Pacific region. However, the authors often base much of their reasoning on the comparison with Greenland ice cores, which are almost half a hemisphere away from Aurora Peak. While such a comparison can be useful, one would not expect fire histories to be similar, due in part to this long distance between the sites. Many fire peaks in the record are single spikes, which may be due to individual fires or to relatively close-by fires. Comparing single spikes between southern Alaska and Greenland is somewhat futile, unless these peaks extend over a longer time period (such as a decade or more) where the peaks can be ascribed to increased fire activity rather than individual fires. The authors do have a good data set, which adds value to both the fire science and paleoclimate communities. However, the conclusions often overreach what information the data can supply.

SPECIFIC COMMENTS: Page 2, Line 24: Do you mean to imply that there are multiple sporadic peaks within the individual years AD 1913 and 2005? If so, then keep the sentence as is. Do you perhaps mean that AD 1913 and 2005 are individual peaks during a time period where there are few other peaks? If so, then please clarify in the abstract.
Response: Thank you for the comment. There are no sporadic peaks within the individual year. By taking the comment, we have corrected the line. Please see line 19 in the revised manuscript (MS).

Page 2, Line 29: Where are the other ice core studies? In possible source regions? In other Northern Hemisphere locations such as the Tibetan Plateau or Greenland? Or general ice core studies of levoglucosan including in the Southern Hemisphere?
Response: Thank you for the comment. Other ice core studies are Svalbard, Akademii Nauk and Tunu. We have added these ice core studies in the revised MS. Please see lines 34-36.

Page 3, lines 42-44 and continuing throughout the paper: Choose to list references in either chronological or alphabetical order, and then remain consistent with this decision throughout the paper.

Response: Thank you for the suggestion. By taking the suggestion, we have cited according to chronological order throughout the MS. Please see the revised MS.

Page 3, lines 46-52: Over what time periods and resolutions do these discrepancies exist? Decades, millennia, etc? Do you mean that the discrepancies are between the Northern and Southern Hemispheres? Are you suggesting that transport differs by hemisphere, and if so, how?

Response: Yes. Millennia, centennials, decadal, and shorter time showed discrepancies. Hence, we have added the following lines in the text. The centennial and/or shorter time scale of trends exhibited different elevated/suppressed concentration trends of p-HBA/vanillic acid during 1600 A.D. and vanillic/p-HBA during 2000-2008 (*Grieman et al., 2018a*). Similarly, Svalbard ice core record (*Grieman et al., 2018a*) showed different elevated/suppressed historical trends/peaks with NEEM- ice core of Greenland (*Zennaro et al., 2018*). These results most likely suggest the changing/shifting contributions of source regions with the different ecosystem of trees, shrubs, and grasses. Please see lines 71-80 in the revised MS.

Page 3, lines 54-58: You mention that there are "a few studies" and then you cite only a single study. There are multiple studies of these biomass burning markers in the Northern Hemisphere including (but certainly not restricted to) the following studies:

Aromatic acids in an Arctic ice core from Svalbard: a proxy record of biomass burning. Grieman, M.M., Aydin, M., Isaksson, E., Schwikowski, M., Saltzman, E.S. (2018). Climate of the Past, 14, 5, 637-651, DOI: 10.5194/cp-14-637-2018

Li, Q., Wang, N.L., Barbante, C., Kang, S., Yao, P., Wan, X., Barbaro, E., Hidalgo, M.D.V., Gambaro, A., Li, C.L., Niu, H.W., Dong, Z.W., Wu, X.B. (2018) Levels and spatial distributions of levoglucosan and dissolved organic carbon in snowpits over the Tibetan Plateau glaciers. Science of the Total Environment, 612, 1340-1347, DOI: 10.1016/j.scitotenv.2017.08.267

Parvin, F., Seki, O., Fujita, K., Iizuka, Y., Matoba, S., Ando, T., Sawada, K.(2019) Assessment for paleoclimatic utility of biomass burning tracers in SDome ice core, Greenland. Atmospheric Environment, 196, 86-94. DOI: 10.1016/j.atmosenv.2018.10.012

You, C., Yao, T., Xu, C. (2019) Environmental Significance of levoglucosan records in a central Tibetan ice core. Science Bulletin, 64, 2, 122-127, DOI: 10.1016/j.atmosenv.2018.

Zennaro, P., Kehrwald, N., Marlon, J., Ruddiman, W.F., Brucher, T., Agostinelli, C., Dahl-Jensen, D., Zangrando, R.,Gambaro, A., Barbante, C. (2015) Europe on fire three thousand years ago: Arson or climate? Geophysical Research Letters, 42, 12, 5023- 5033, DOI: 10.1002/2015GL064259

Response: By taking the suggestion, we have added the following references through out the revised MS.

Parvin et al., 2019; You et al., 2019; Grieman et al., 2017; 2018a,b; Li et al., 2018; Zennaro et al., 2018; and Legrand et al., 2016. Please see lines 58-61. Thank you for providing these references.

Page 3, lines 58-61: Do you mean that this is the first time that all three specific biomass burning tracers (levoglucosan, dehydroabietic and vanillic acid) were analyzed together in an ice core? Or do you mean that this is the first time that Kawamura et al. investigated these three markers.
Response: We have deleted the term of "first" in revised MS. Please see line 91-93.

Page 4, Line 62: Please be clear as to which three compounds you are investigating in the paper.
Response: By taking a comment, we wrote clearly about three compounds. In this paper we reports three compounds, that is, levoglucosan, dehydroabietic acid and vanillic acid) in an ice core. Please see lines 91.

Page 4, Line 63 and continuing throughout the paper: Acronyms can tend to interrupt the flow of reading instead of helping. Use the name "Aurora Peak" throughout the rest of the paper instead of the acronym "APA."
Response: Thank you, by taking the reviewer's comment we have used the name "Aurora Peak" throughout the paper. Please see the revised MS.

Page 4, Line 64 and continuing throughout the paper: All dates must include C.E. or A.D.
Response: Thank you. By taking the reviewer's comment, we have added all dates are in A.D.

Page 4, Line 71 and continuing throughout the paper: Many of your references contain both the numbers from your citation software, followed by the written names of the references. Carefully check the document and omit all numbers related to the references. (In this case, you would change "Eastern Europe2 (Kawamura et al., 2012)" to "Eastern Europe (Kawamura et al., 2012)".
Response: Thank you. We have corrected throughout the revised MS.

Page 4, Line 80: Here you cite Tsushima, 2014 and Tsushima et al., 2014. Your references state that both were published in 2015. Please double-check these dates.
Response: Sorry for the mistake. We have corrected the dates, Tsushima, 2015 and Tsushima et al., 2015. Please see line 114.

Page 4, Line 86: Pokhrel et al., 2015b does not exist in your reference list. Instead, you cite a paper that was submitted to ES&T in 2016. In a search for this paper on "Web of Science" this paper was not published. It is not acceptable to use unpublished – and possibly rejected – work as a reference.
Response: Thank you, we have deleted this reference in the revised MS.

Page 4, Lines 62-72: This paragraph ends abruptly. The authors state the aim of the study at the beginning of the paragraph, then dive into specifics, and then abruptly stop. The study goal becomes lost in this paragraph structure. Please revise.

Response: Thank you for the suggestion. By taking the reviewer's comment, we have added following lines in the revised MS. "This study covers 1665-2008 A.D. to better understand the historical atmospheric transport variability between the western North Pacific region (*Kawamura et al., 2012*) and eastern North Pacific region (this study) from source regions as well other ice core studies (e.g., Greenland, Svalbard and Akademii Nauk in the NH). The results of this study can further disclose the database of levoglucosan, dehydroabietic and vanillic acids from the alpine glacier in the North Pacific rim to explore their possible sources, origin, long and short-range atmospheric transport, ecological changes and climate variability in the NH. Please see lines 91-101 in the revised MS.

Page 4, Lines 74-81: What evidence do you have that the ice core is 274 y BP at the depth of 180 m other than the annual layer counting? Cite Tsushima, 2015 a and b here. (Your citation of Tsushima, 2014 is incorrect as the papers you cite were published in 2015. Also, one of the Tsushima papers should be labeled "a" and the other should be "b"). In the Pokhrel, 2015 dissertation abstract, the age at 180 m is cited as 343 y BP. Of course, with new knowledge, depth-age scales can change. However, what DID change? Did you acquire independent dates?
Response: Thank you, by taking reviewer's suggestion, we have cited Tshushima, 2015 and Tsushima et al., 2015. We did not acquire independent dates. Dates were measured by another group of our Institute of Low Temperature Science, Hokkaido University. Hence, we cited her paper. Please see line 114.

Page 4, Lines 80-81: Do you mean that 5-10 mm was shaved off the outside section of the core? Off all sections? How did you clean the ceramic knife?
Response: Yes, we shaved off 5-10mm for all the sections. We cleaned ceramic knife 3 times by using organic free pure water (MiliQ water), 3 times by methanol (MeOH), 3 times by dichloromethane (DCM) and 3 times by mixture of 2:1 DCM and MeOH. Please see lines 117-122.

Page 4, Line 84: What kind of container? LDPE? Glass? What size? Were these containers cleaned? If so, how?
Response: We used IWAKI and/or PYREX's clean glass beaker of 1000 mL. First, we baked those containers for 12 hours at 450°C and then cleaned them three times by using organic free pure water (MiliQ water), 3 times by methanol (MeOH), 3 times by dichloromethane (DCM) and 3 times by mixture of 2:1 of DCM and MeOH, respectively. Please see lines 122-128.

Page 4, Line 85: What do you mean by a "standard clean room"? A Class 100? A Class 10,000?
Response: Thank you. We just used a clean room (level-2). Please see line 124.

Page 4, Lines 87-88: Do you mean one quarter of the ice core by depth or by circumference? You mention that the sampling frequency was approximately 40% of the entire ice core. However, if you are taking 25% of the core, then how do you get a sampling frequency of 40%? If you are sampling by circumference, then you would have a continuous record. If you are sampling by depth, then you would have approximately 50% of the core. Are there locations in the core that you were not able to sample due to breakage, etc? If so, then note these locations.
Response: Thank you for the question. We used one-quarter of the ice core by circumference. Only 40% of samples were available to measure for biomass burning (BB) tracers for our group. It does not have any special reasons. There was no breakage ice chronology. Please see lines 117, 128-129.

Page 4, Line 102: What are the "authentic standards" that you used? What concentrations? Where did you purchase the standards? Did you use any isotopically-marked standards? Did you include the standards in the samples as internal standards? Methods and materials: Do you have any lab blanks? Do you have any procedural blanks? If so, do you have any way for accounting for the concentrations of the three analytes in your blanks? If you do not have any blanks, what sort of QA/QC measures did you apply? What is the LOD for the analyzed compounds? Was each sample analyzed in triplicate (Page 5, Line 105)? Or were only three samples analyzed in triplicate?
Response: Thank you very much for the comment. The authentic standard contains levoglucosan (5.5 ng/μL), dehydroabietic acid (4.7 ng/μL), and vanillic acid (4.2 ng/μL), which was purchased from Wako, Japan. We did not use any isotopically marked standards. Instead, n-tridecane ($C_{13}H_{28}$) is used as an internal standard. We did not find levoglucosan, dehydroabietic acid, and vanillic acid in lab blank as well as procedural blanks. Only one sample was used for duplicate analysis. LOD for analyzed compounds 0.002 to 0.005 ng/kg-ice. Please see lines 145- 159.

Page 4, Line 104: You mention that analytical details are included in Simoneit et al., 2004, yet you do not include this paper in your references. A literature search demonstrates two options where Simoneit et al., 2004 investigates levoglucosan, etc. However, neither of the two possible Simoneit et al., 2004 papers nor Fu et al., 2008
(who you mention as another paper that contains the full method details) include essential information such as the m/z, the amount of time analyzing each m/z, etc. While you can still cite these papers, you still do need to include the primary information of the method.
Response: By taking the reviewer's suggestion, we have added detail methods, including m/z value in the revised MS. Please see lines 130-159.

Page 6, Line 116: When you state an "important fraction", please mention how this fraction is important. Due to the volume? Due to the fact that anhydromonosccharides were produced by biomass burning?
Response: Thank you, we have deleted the phrase in the revised MS.

Page 6, Lines 125-128: Here you argue that Figure 1 demonstrates that Aurora Peak is far away from any biomass burning sources, but in Figure 5 you demonstrate that there are fire sources near the peak. Explain this discrepancy.
Response: We have deleted this line in the revised MS. To make a clear, we have added new figure of air mass back trajectories (BTs) together with fire counts. The results of BT and fire counts showed that Alaska was influenced by biomass burning from Siberia, Russia, Europe, China, Mongolia, Canada, and Japan. Please see Figure 7a-f and lines 160-173.

Page 6, Line 119: Here, you state that levoglucosan is only produced at temperatures above 300ïC´ ˇr C, and cite references from 1984 until 2002. However, more recent literature (Kuo et al., 2011) states that levoglucosan and its isomers are only produced at temperatures up to 350ïC´ ˇr C. Explain this discrepancy. The citation for Kuo et al. is the same as you use later on the same page:

Kuo, L-J., Louchouarn, P., Herbert, B.E. (2011) Influence of combustion conditions on yields of solvent-extractable anhydrosugars and lignin phenols in chars: Implications for characterizations of biomass combustion residues. Chemosphere, 85, 797-805 doi:10.1016/j.chemosphere.2011.06.074

Response: Thank you for the comment; we have added the following lines in the revised MS. “Recently, Kuo et al. (2011) further reported that levoglucosan and its isomers produced at temperature up to 350°C.” Please see lines 183-184.

Section 3.1: What evidence do you have that the fact that mannosan and galactosan are consistently below the limit of detection is due to these isomers not being present, versus to these isomers simply not being detectable by the analytical method? As mannosan is below the detection limit, the statement that “Thus, levoglucosan/mannosan mass ratios (L/M) could be relatively high” does not make sense. You would have to divide your levoglucosan results by zero. As you do not have quantifiable numbers for mannosan and glacactosan, the paragraph (Page 7, Lines 143-151) does not add value to the paper, and can be omitted.
Response: Thank you for the question. We have deleted this paragraph in the revised MS because mannosan and glacactosan were not detected in this study.
We used the same method reported by Kawamura et al. (2012), who already reported these species. We believe that this method is suitable to detect mannosan and galactosan.

Page 8, Lines 171-174: Many studies have wide ranges for the atmospheric lifetime of levoglucosan. The Hennigan et al., 2010 study is on the extremely low end of these calculations. Please include other studies and results to give a more accurate range.
Response: Thank you. By taking a reviewer’s comment, we have modified sentences as follows. “Although levoglucosan may not be as stable as previously thought in the atmosphere (Hoffmann et al., 2010; Fraser and Lakshmanan, 2000), its concentrations are

not seriously influenced during the transport for several days (Hoffmann et al., 2010; Mochida et al., 2010).

However, degradation of levoglucosan depends upon the levels of OH radicals (Hennigan et al., 2010), which are seriously affected by relative humidity of the atmosphere and air mass aging during long range atmospheric transport from East and North Asia to southern Alaska (Lai et al., 2014; Hoffman et al., 2010). We have added new references." Please see lines 211-218.

Page 8, Line 175 to Page 9, Line 189: (i) Do you mean that the source regions are southern Alaska as well as the possible source regions that are listed in lines 181- 182? If so, then why do you separate southern Alaska? (ii) Do you mean that the heavy forest fires in eastern Siberia occur now, or occurred in the past, or both? (iii) Why do you compare your regional record to global biomass burning? (iv) Do you have a regional biomass burning record from charcoal or other data? (v) Do you have any indication of land-use change in eastern Siberia in the 1840s?

Response: Thank you.

(i) This time we performed back trajectory analysis together with fire counts. Hence, the sources are Siberia, East Asia, Europe, Canada, higher latitude of Alaska. Hence, we reorganized the lines. Please see lines 223-225.

(ii) It occurred in the past (e.g., Ivanova et al., 2010). Please see line 225-228 in the revised MS.

(iii) We also got at least nine higher peaks of levoglucosan (Figure 2a) during the same time as 1750s-1840s (*Marlon et al., 2008*). Hence, we compare to global biomass burning.

(iv) We do not have charcoal data. Back trajectory analysis showed that Alaska was influenced from Europe, Russia, Siberia, East Asia, and Canada. Hence, we compare with global biomass burning.

(v) Marlon et al. (2008) reported it. Hence, we have cited this reference in the revised MS. Please see line 229-231.

Page 9, Lines 190-200: This paragraph is illogical. Please omit the sentence "We did not detect significant concentrations of any isomers as we have discussed above" as discussing isomer ratios does not fit into this paragraph.

Response: By taking the reviewer's comment, we have deleted the sentences in the revised MS.

Section 3.1: (i) Are these spikes individual points or are they multiple points consecutively in the ice core? (ii) How can you determine if the spikes indicate a close fire, versus a fire that is farther away? (iii) Do the spikes indicate fire intensity?

Response: Thank you for the questions.

(i) These spikes are the individual point in the ice core.

(ii) We cannot determine it directly. However, by using back trajectory analysis together with fire counts (2002-2007) we can indicates that long-range atmospheric transport is important in Alaska.

(iii) Yes, spikes also may indicate fire intensity.

Page 9, Lines 201 to 204: The argument "These suggest that ice core NH4+ has common sources in the circumpolar regions" does not logically follow from the preceding sentence.
Response: Thank you, we have deleted the ionic part in the revised MS.

Pages 9 and 10: The distances between Alaska and Greenland is thousands of kilometers. (i) Do you have other evidence than similar spikes of NH4+ between Mt Logan, GISP 2, and 20D to suggest "that ice core HN4+ has common sources in the circumpolar regions?" (ii) Are these spikes just visually the same, or is there some statistical test done to determine that these spikes correlate? (iii) Are the spikes just individual points, or are they peaks over decades? The following review paper investigates boreal fire source regions and the atmospheric transport, with implications for your assumptions on pages 9 and 10. Essentially, it would be difficult, although not impossible for the fire source regions to be the same for both Alaskan and Greenland ice core records:
Legrand, M., McConnell, J., Fischer, H., Wolff, E.W., Preunkert, S., Arienzo, M., Chellman, N., Leuenberger, D., Maselli, O., Place, P., Sigl, M., Schuepbach, Flannigan, M. (2016) Boreal fire records in Northern Hemisphere ice cores: a review. Climate of the Past, 12, 2033-2059, doi:10.5194/cp-12-2033-2016.

Response: Thank you very much. The common source regions for these higher spikes could be East Asia, Eastern Russia, Siberia, higher latitudes of Alaskan regions, and Canadian regions for those above-mentioned study sites. We assume that common source regions contributed the similar higher spikes for Mt. Logan, Greenland and Aurora Peak of Alaska.

We observed the similar higher spikes during the same periods for these sites. Except for the similar higher spikes, we do not have more evidence. The spikes are visually same. We did not perform the correlation analysis. Hence, we have added a few lines. Please see lines 259-260 and 283-288.

Section 3.1: Why is Whitlow et al., 1994 your primary reference when the research into boreal forest fires and ice core records has increased substantially in the past 25 years?
Response: Thank you for the comments, this time we have added many new references. Please see the same section.

Pages 10 and 11: Lines 232-239: Would you like to say that the fires after 1900 only affect Mt. Logan and not Aurora Peak? Why is Aurora Peak more similar to Greenland records than to other Alaskan records? Please clarify.
Response: Thank you very much. Yes, I would like to say that after 1900, fires affect more to Mt. Logan than Aurora Peak. In 19^{th} century, the concentration of levoglucosan is drastically decreased in Alaska. Greenland and Alaska have common source regions of Siberia, Eastern Russia. Please see lines 297-301.

Page 11, Lines 245-246: What mechanism do you propose for increased dilution and/or scavenging of biomass plumes after the 1830s? Would this mechanism affect the entire Arctic or just southern Alaska?
Response: Thank you. "The mechanism could be dry and wet scavenging, diffusion, and degradation by hydroxyl radicals in the atmosphere during long-range atmospheric transport." Hence, we have added above lines to revised MS. Please see lines 291-295.

Page 11, Lines 245-247: In what ice core(s) do the see the difference in the concentrations? Is this a comparison between Aurora Peak and Greenland ice cores? If so, why would you expect a similarity over half a hemisphere of distance?
Response: Thank you for the comment. We have modified the sentence as below in the revised MS. "Mt. Logan, Svalbard, Tunu of Greenland and Aurora have common source regions, e.g. Russia and/or Siberian forest as well the North America/Canadian forest." Please see lines 297-301 and Figure 6a-e.

Page 11: Lines 247-249: You state "These special events further suggest that Alaskan glaciers cannot preserve most biomass burning events in the circumpolar regions, which occurred in the source regions of Siberia and North America". Do you mean that the combination of distance and atmospheric transport means that most fires in Siberia and North America will not be recorded in Alaska mountain glaciers? Do you mean that the difference between the Alaskan and Greenland ice core biomass burning records suggest that the Alaskan glaciers are not as good of receptors as the Greenland ice sheet?
Response: We have deleted these lines in the revised MS.

Page 11, Lines 257-258: By mentioning the Little Ice Age, do you mean to imply that the cooler weather influenced the decreased biomass burning? Do you have any evidence or records of decreased temperatures in Siberia during this time period?
Response: Thank you very much for the comment. We rephrased this sentence in the revised MS. Please see lines 465-473.

Page 13, line 287-289: Do you mean that the East Asian regions are more important for regional levoglucosan production or that they are more important as a source of levoglucosan for Aurora peak? You do go on to discuss this point further in the next few paragraphs, but as this is the first time that the reader is exposed to this idea, it is better to be clear from the onset.
Response: Yes, correlation of levoglucosan with dehydroabietic and vanillic acids from 1920 to 1977 A.D. are not significant (τ=0.11, 0.14) but vanillic vs. dehydroabietic acid showed significant correlation (0.41, $p<0.01$), suggesting different source region for levoglucosan. Please see lines 358-364.

Again, the significant correlation (Figure 3a-c) between dehydroabietic acid (except for 2005) and vanillic acid (τ= 0.60, $p<0.01$) is better than the correlations of levoglucosan with dehydroabietic (except for 1981 and 1986) acid (0.30) and vanillic acid (0.21) after the

Great Pacific Climate Shift (GPCS) that is, 1977-2007 AD. Please see line 420-423 and Figs. 3.

Backward trajectories analysis (500 hPa) of air masses (2002-2007 AD) together with fire counts, also showed that source regions are also Mongolia, China and Japan (Figure 7a-f).

Pages 14 and 15: Why would the long-range atmospheric transport be insignificant? It may just be that regional transport overwhelms the long-range signal from the 1920s until the present, but the same amount of long-range transport may occur. What do you mean that the concentrations "are secure"?
Response: Correlation of levoglucosan with dehydroabietic and vanillic acid from 1920 to 1977 A.D. are not significant (Kendall's τ=0.11, 0.14) but vanillic vs. dehydroabietic acid showed significant correlation (0.41, $p<0.01$), suggesting different source region for levoglucosan. Please see lines 358-364.

Again, the significant correlation (Figure 3a-c) between dehydroabietic acid and vanillic acid (τ= 0.60, $p<0.01$) is strong than those of insignificant correlations of levoglucosan with dehydroabietic acid (0.30) and vanillic acid (0.21) after the Great Pacific Climate Shift (GPCS) that is, 1977-2007 AD. Please see line 420-423.

In addition, from 1980s to onwards, trends of dehydroabeitic acid is increasing (similar to Kamchatka ice core records) and concentration is higher than levoglucosan. These results strongly suggest that they have different sources. Hence, for the dehydoabeitic acid and vanillic regional transport overwhelms the long range atmospheric transport.
Hence, we added following lines to revised MS. "….regional transport overwhelms the long-range atmospheric transport….." Please see lines 383-385.

We have deleted the word "secure" in the revised MS.

Pages 14 and 15: Why did you choose to do a point to point correlation of data from a time series? The data are definitely skewed, with the majority of the data with low concentrations and then a few separate spikes. Why did you not choose other types of correlations that may be more applicable? What is the statistical level of correlation of each of these factors?
Response: Yes, we agreed with reviewer's comment. By taking the comment, we have added non parametric Kendall's correlation (τ) and explained the results accordingly. Please see Figures 3 and 4.

Page 17, Line 400: In what way do the forest fire signal depend on the source region? Do they depend on proximity to the source? Do they depend on the type of vegetation burned in the source region?

Response: Thank you very much. Yes, the forest fire signals depend on the source region and proximity to the source, and types of vegetation. Hence, we have added one sentence in the revised MS. Please see lines 561-566.

Page 17, Lines 401-403: Your paragraph is better without this sentence. Please remove.
Response: Thank you. We have deleted the lines.

Figure 5: Why do you investigate the MODIS fire spots over different areas for each year? For example, the 2004 plot stops at ~45 degrees N, while the 2006 plot stops at ~ 32 degrees N. Why do you include much of the United States, if regions south of 45 degrees north are unlikely to be a source region? If Siberia is a major source region, why did you not also investigate Siberia with any available data?
Response: Thank you. By taking comments, we have added MODIS fore spots for major source region together with cluster analysis. Please see Figure 7a-f.

TECHNICAL CORRECTIONS: Title: Place "the" before "1660s" in the title
Response: Corrected. Please see title.

Page 2, Line 18: Change "melt" to "melted"
Response: This sentence was deleted.

Page 2, Lines 24 and 25: Change "there are few discrepancies of higher spikes among them after the 1970s" to "there are a few discrepancies of higher spikes especially after the 1970s".
Response: The sentences were deleted.

Page 1, Line 27: Place "as well as" before "other higher plants"
Response: This sentence was deleted.

Page 2, Line 29: Change "regions of southern Alaska, being different from previous ice core studies" to "regions of southern Alaska. These results differ from previous ice core studies."
Response: The phrase was deleted.

Page 2, Line 34 and Page 17, Line 398: The word "gleaming" is wonderful, and I am sorry to suggest replacing this word with more boring options. Unfortunately, it is not quite clear what you would like to suggest with this word. Do you mean substantial? Clear? Definitive? If so, please use one of these words.
Response: These words are deleted.

Page 3, Line 39: Replace "provide the" with "archive"
Response: Corrected. Please see line 51.

Page 3, Line 42: Omit "which are reported elsewhere"

Response: Omitted.

Page 3, Lines 45-46: with “have some extent on climate change effect” do you mean to say “may affect climate change”? If so, then replace the phrase.
Response: Corrected. Please see line 49.

Page 3, Line 54: Place “a” before “pyrolysis” Page 4, lines 66-67: Change “Particularly, 10 day backward trajectory” to “Particularly, 10-day back trajectories”
Response: These words are deleted.

Page 4, Lines 85-86: By “All steps are followed as reported previously prior to analysis (Pokhrel, 2015; Pokhrel et al., 2015b)” do you mean “All analytical steps are previously reported in Pokhrel, 2015 and Pokhrel et al., 2015b”?
Response: We added references of Fu et al., 2011 and Kawamura et al., *2012* with some explanation in the revised MS. Please see section 2.

Page 5, Line 89: Change “melt” to “melted” Page 5, Line 90: Change “shape” to “shaped”
Response: Corrected. Please see lines 130 and 131.

Page 5, Line 93: Choose to use either chemical formulas or names, and then be consistent throughout the paper.
Response: Corrected throughout the section 2.

Page 5, Line 94: Change “reported previously” to “previously reported”
Response: Deleted these words in the revised MS.

Page 5, Line 107: Change “were” to “was” Page 5, Line 108: Change “were” to “was”
Response: Deleted.

Page 5, Line 108: Omit “traject” before “compounds”
Response: Corrected to “target”. Please see line 156.

Page 5, Line 109: I am sorry, but I do not understand what you would like to say by “physical functioning fire smoldering spot”. Please change this phrase.
Response: Deleted these words in the revised MS.

Page 6, Line 116: Place “to” before “an important fraction”.
Response: Deleted this line in the revised MS.

Page 6, Line 125: Omit “(i.e., distribution)”
Response: It is removed.

Page 6, Line 128: Omit “the” before “Aurora Peak” and replace “the” with “any” before “biomass burning” Page 7, Line 144: Change “sifnificant” to “significant”

Response: Thank you. Both are deleted.

Page 7, Line 160: This is the first time that you have used the acronym “BB”. Replace with “biomass burning” and do not use the acronym.
Response: Thank you, deleted.

Page 8, Line 162: Replace “didn’t” with “did not”.
Response: Deleted.

Page 8, Line 175: Replace “around” with “the”
Response: Deleted.

Page 9, Line 192: Use the full word “levoglucosan” rather than “Lev”.
Response: Thank you. Corrected throughout the MS.

Page 8, Line 183 and Page 9, Line 198: Replace “borel” with “boreal” Page 9, Line 204: Replace “got” with “obtained”
Response: Thank you. We have corrected them and deleted this word: got. Please see lines 226, 246, 357.

Page 10, Line 212: Change “is consistent to” to “is consistent with” Page 11, Line 238: Replace “only the exception” with “the only exception”
Response: Thank you very much. Please see lines 254 and 281 in the revised MS.

Page 11, Line 240: Replace “Above results and discussion suggest the subsequent evidences” with “The above results suggest”
Response: Corrected. Please see line 289 in the revised MS.

Page 11, Line 242: Replace “souhtern” with “southern”
Response: Corrected. Please see line 291.

Page 11, Line 251: Unfortunately, “heavy” does not describe forest fires. Do you mean intense? Do you mean widespread?
Response: Thank you. I mean both, intense and widespread. I have added both words in the revised MS. Please see line 304.

Page 11, Line 249: Replace “Siberian” with “Siberia”
Response: Corrected.

Page 11: Line 248: Replace “can not” with “cannot”
Response: Deleted.

Page 11, Line 254: Replace “declined” with “declining”
Response: Corrected. Please see line 308.

Page 12, Lines 280-283: Change to “These results suggest that biomass burning plumes of pine, larch, spruce and fir trees in Siberian regions (Kawamura et al., 2012: Ivanova et al., 2010) have a substantially larger influence on Kamchatka, southeastern Russia than on southern Alaska”.
Response: Thank you very much. We have replaced it. Please see lines 347-350.

Page 12, Line 286: Change “borel” to “boreal”
Response: Deleted.

Page 13, Line 296: Change “discrepancy” to “discrepancies”
Response: Corrected. Please see line 371.

Page 13, Lines 297 to 298: Change “Kamchatka showed gradual increase after the 1950s” to “Dehydroabietic acid concentrations gradually increased in the Kamchatka ice core after the 1950s”.
Response: Corrected. Please see lines 372-373.

Page 13, Line 305: Change “doesn’t” to “does not”. Page 14, Line 326: Change “conifer rich” to “conifer-rich”
Response: Deleted this phrase. Corrected, Please see line 406 in the revised MS.

Page 15, Line 347: Remove “from” before “climate driven”
Response: This line is deleted in the revised MS.

Page 15, Line 349: Change “could be” to “may be” Page 16, Line 369: Replace “constitute” with “constituent”
Response: These words are deleted in the revised MS.

Page 16, Lines 377-384: You only use the acronym “NPR” three times. It is much better to use the words “North Pacific Rim” than an acronym that introduces confusion. Please use the words for this phrase rather than the acronym throughout the paragraph.
Response: Corrected through out in the revised MS.

Page 17, Line 395: Replace “with early study” with “than a previous study” and then cite the study in the sentence. Figure 1: Place “a” before “180-meter”. This figure does not need a citation unless you are using the exact figure as in your earlier work.
Response: Thank you, we have deleted it.
We place “a” before 180-meter. Please see the figure caption. We have modified Figure 1 in the revised MS.

Ice core records of levoglucosan, dehydroabietic and vanillic acids from Aurora Peak in Alaska since the 1660s: A proxy signal of biomass burning activities in the North Pacific Rim

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Abstract

A 180 m-long (343 years) ice core was drilled in the saddle of Aurora Peak in Alaska (63.52°N; 146.54°W, elevation: 2,825 m) and studied for biomass burning tracers. Concentrations of levoglucosan and dehydroabietic and vanillic acids exhibit multi-decadal variability with higher spikes in the 1678, 1692, 1695, 1716, 1750, 1764, 1756, 1834, 1898, 1913, 1966 and 2005 A.D. Historical trends of these compounds showed enhanced biomass burning activities in the deciduous broad leave forests, boreal conifer forests and/or tundra woodland and mountain ecosystems before the 1830s and after the Great Pacific Climate Shift (GPCS). The gradually elevated level of dehydroabietic acid after the GPCS is similar to p-hydroxybenzoic acid (p-HBA) from Svalbard ice core, suggesting common climate variability in the Northern Hemisphere. The periodic cycle of levoglucosan, which seemed to be associated with the Pacific Decadal Oscillation (PDO), may be more involved with the long-range atmospheric transport than other species. These compounds showed significant correlations with global lower tropospheric temperature anomalies (GLTTA). The relations of the biomass burning tracers with PDO and GLTTA in this study suggest that their emission, frequency, and deposition are controlled by the climate driven forces. In addition, historical trends of dehydroabietic and vanillic acids (burning products of resin and lignin, respectively) from our ice core demonstrate the northern hemispheric connections to the common source regions as suggested from other ice core studies from Svalbard, Akademii Nauk and Tunu Greenland in the Northern Hemisphere.

(Words: 240)

1. Introduction

Biomass burning tracers (e.g., levoglucosan, dehydroabietic, vanillic, p-droxybenzoic, and syringic acids) are ubiquitous in the atmosphere and well deposited on ice sheets as snow particles (i.e., precipitation) (Muller-Tautges et al., 2016; Grieman et al., 2018a,b; Shi et al., 2019). Previously, ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}) were used to understand the atmospheric signals of biomass burning and/or the Pioneer Agriculture Revolution (PIA-GREV) in the Northern Hemisphere (Holdsworth et al., 1996; Legrand and Mayewski, 1997; Legrand et al., 2016). For instance, a signal of biomass burning is ammonium (e.g., $[NH_4]_2SO_4$) in snow particles, which is a constituent of forest fire smoke (Holdsworth et al., 1996; Tsai et al., 2013). Biomass burning activities such as forest fires and residential heating may affect climate change (Legrand and De Angelis, 1996; Savarino and Legrand 1998; Gambaro et al., 2008; Keywood et al., 2011).

Ice core records archive the long-term changes in deposition and concentration of organic (e.g., biomass burning tracers, ethane, formate, acetate, dicarboxylic acids, pyruvic acid and α-dicarbonyls) and inorganic species (e.g., NH_3^+, SO_4^{2-}, NO_3^-, K^+ and NO_2^-) (Yang et al., 1995; Legrand and Mayewski, 1997; Andreae and Merlet, 2001; Kaufmann et al., 2010; Lamarque et al., 2010; Wolff et al., 2012; Kawamura et al., 2012; Kehrwald et al., 2012; Legrand et al., 2016; Shi et al., 2019). Many studies have shown that there are some discrepancies of temporal and spatial biomass burning activities in ice core proximity records (Legrand et al., 1992,1996; Kaplan et al., 2010; Kawamura et al., 2012; Grieman et al., 2015; Rubino et al., 2016; Legrand et al., 2016; Grieman et al., 2017; Zennaro et al., 2018; Li et al., 2018; Grieman et al., 2018a,b; You et al., 2019) in both Northern and Southern Hemisphere (NH/SH).

Previous proxy records of biomass burning activities from Lomonosovfona, Svalbard (Grieman et al., 2018a) showed different trend between vanillic acid and p-hydroxybenzoic acid (p-HBA) within the same ice core sample. Interestingly, ice core records of NEEM (Zennarao et al., 2014; 2018) demonstrated a human impact on the climate system since four thousand years ago. A different circumpolar region in the NH has a different atmospheric airmass circulation with different results of biomass burning tracers such as levoglucosan, vanillic, dehydroabietic and syringic acids, ethane, ammonium and other carboxylic acids, suggesting potential discrepancies of origin, transport, and deposition of these compounds on the ice crystals.

These discrepancies of biomass burning tracers in different ice core records may suggest the different glacio-chemical cycles in the NH and SH throughout decadal to centennial and even millennia. For example, centennial and/or shorter time scale of trends exhibited different elevated/suppressed concentration trends of p-HBA/vanillic acid during 1600 A.D. and vanillic/p-HBA during 2000-2008 A.D. (Grieman et al., 2018a). Similarly, Svalbard ice core record (Grieman et al., 2018a) showed different elevated/suppressed historical trends/peaks from NEEM- ice core of Greenland (Zennaro et al., 2018). These results most likely suggest the occurrence of changing/shifting contributions of source regions with the different ecosystem of trees, shrubs, and grasses to the sampling sites.

There are a few ice core studies of biomass burning-derived specific organic tracers, including levoglucosan that is a pyrolysis product of cellulose and hemicellulose and other sugar compounds such as mannosan and galactosan, as well as dehydroabietic and vanillic acids which are biomass burning products of resin and lignin, respectively (Kawamura et al., 2012; Legrand et al., 2016; Grieman et al., 2017; Zennaro et al., 2018; Li et al., 2018; Grieman et al., 2018a,b; You et al., 2019).

Kawamura et al. (2012) reported specific biomass burning tracers (levoglucosan, dehydroabietic and vanillic acid) for an ice core (1693-1997 A.D.), collected from the Kamchatka Peninsula (56º04'N, 160º28'E, Elevation: 3,903 m) in the western North Pacific Rim.

In this paper, we report levoglucosan, dehydroabietic acid and vanillic acid in an ice core collected from Aurora Peak of southern Alaska, an inland site facing to the northeast of Pacific Ocean. This ice core covers 1665-2008 A.D., which can help to better understand the historical variability in the atmospheric transport of biomass burning tracers between the western North Pacific (Kawamura et al., 2012) and eastern North Pacific (this study). We also compare the present results with other ice core studies from Greenland, Svalbard and Akademii Nauk in the NH. The results of this study can further disclose the database of levoglucosan, dehydroabietic and vanillic acids from the alpine glacier in the North Pacific Rim to explore their possible sources, origin, long- and short-range atmospheric transport, ecological changes and climate variability in the NH.

2. Materials and Methods

An ice core (180.17 m deep, 343 years old) was drilled in the saddle of the Aurora Peak of southern Alaska (location: 63.52°N, 146.54°W, elevation: 2,825 m, see Fig. 1 for sampling site). The annual mean temperature at the site was minus 2.2°C, which matched to the temperature of 10 m depth in the borehole-ice. The annual accumulation rate of snow is 8 mm yr^{-1} since 19 century and 23 mm yr^{-1} after the Great Pacific Climate Shift (GPCS, cold water masses were replaced by warm water since 1977, e.g., Meehl et al, 2009). The 180 m long core was divided into ~50 cm pieces and directly transported to the laboratory of the Institute of Low

Temperature Science, Hokkaido University, Japan and stored in a dark, cold room at -20ºC until analysis.

The ice core ages were determined by using annual counting of hydrogen isotopes (δD) and Na^+ seasonal cycles (Tshushima, 2015; Tsushima et al., 2015) with tritium-peak reference horizons of 1963 and 1964 and volcanic eruptions of Mt. Spurr and Mt. Katmai in 1992 and 1912 with dating error was ±3 years of 0.02 m resolution. These ice core samples (50 cm long, one-quarter cut by circumference) were mechanically shaved off (~5 – 10 mm thickness of the out core surface) on a clean bench at -15°C in a cold room. A ceramic knife was used to avoid a possible contamination during sample collection. We cleaned ceramic knife (total 12 times) three times by using organic free pure water (MiliQ water), methanol (MeOH), dichloromethane (DCM) and a mixture of 2:1 of DCM and MeOH. These scraped ice samples were placed in a clean glass jar (Iwaki Glass, 1000 mL) for 24 hours with aluminum foil as a cap cover in a level-2 clean room, After 24 hours, these shaving ice core samples were kept at room temperature (ca. 25°C) to which small amount (ca. 10 mg) of $HgCl_2$ was added (Pokhrel, 2015). Finally, the thawed sample was transferred into a 800 ml pre-cleaned brown glass bottle and stored at 4°C. The clean glass jars and bottles were pre-heated at 450°C for 12 hours. The total number of ice core sections was 147 with sampling frequency of ~40% of ice core.

These melted ice core samples (150 mL) were concentrated to almost dryness using a rotary evaporator under a vacuum in a pear shaped flask (300 ml) and extracted by a mixture of DCM/MeOH (2:1) using an ultrasonic bath. The extracts were transferred to 1.5 mL glass vial and dried under a nitrogen stream. Extracts were derivatized with 99% N, O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) + 1%

trimethylchlorosilane (TMCS) and 10 μl of pyridine at 70°C for three hours (Fu et al., 2011; Kawamura et al., 2012). Before injection to gas chromatography (GC)/mass spectrometry (MS), known volume of internal standard (n-C_{13} alkane) was added. GC peaks were analyzed by GC/MS: a Hewlett–Packard Model 5973 MSD coupled to a HP 6890 GC using a capillary column (HP-5MS, 30 m×0.32 mm I.D., 0.25 μm film thickness) installed with a split/splitless injector. The GC oven temperature was programmed from 50°C (2 min) to 120°C at 30°C/min, and then to 300°C at 6°C/min and maintained at 300°C for 20 min. Helium was used as a carrier gas. The GC/MS was operated on a scan mode (m/z=50-650) with an electron impact mode at 70 eV (Pokhrel et al., 2016).

Fragment ions at m/z = 217, 204 and 333 for levoglucosan, m/z = 239 for dehydroabietic acid and m/z = 297/312/267 for vanillic acid were processed on the Chemistation software and used for quantification. Peaks were further confirmed by comparing the mass spectra with those of authentic standards and the mass spectral data in the NIST/Willey library. An aliquot of authentic standard solution (10 μL) containing levoglucosan, dehydroabietic acid, vanillic acid and syringic acid (5.5, 4.7 and 4.2 ng/μL, respectively) was spiked to organic free Milli-Q water (200 ml) placed in the pear-shaped flask. The water sample was concentrated and dried by the procedure described above. The concentrates were derivatized with BSTFA and peaks were analyzed by GC/MS. The recoveries of the spiked samples of levoglucosan, dehydroabietic acid, and vanillic acid were more than 83%. Duplicate analyses were conducted to check analytical error of target compounds, which were less than 9%. Laboratory blanks was measured using Milli-Q water (200 ml). The procedural blanks showed no detectable peaks of these compounds. Detection limits of these species were 0.002-0.005 ng/kg-ice.

We performed cluster analysis for 10 days backward trajectories at 500 hPa for 2002 to 2007 (Fig. 7a-f) computed for every 6 hours, which disclose that long-range atmospheric circulation was significant in the study site of Aurora Peak. To identify the possible source regions of biomass burning events, we prepared annual composite maps (2002 to 2008 AD) of the Moderate Resolution Imaging Spectroradiometer (i.e. MODIS) effective hot spot (Fig. 7a-f) from the Earth Observing System Data and Information System (EOSDIS) using the Terra and Aqua satellites of NASA (https://earthdata.nasa.gov/data/near-real-time-data/firms/active-fire-data). The 10 days backward trajectory analysis from 2002 to 2007 showed that Aurora Peak received air masses from the North Pacific Ocean, East Asia, Siberia, Europe, Canada, and higher latitude of Alaska (Fig. 7a-f). Similar sources were reported using 10-days backward trajectory from 1992-2002 (>300 hPa) (Yasunari and Yamazaki, 2009). The Kamchatka Peninsula also receives air masses from China, Mongolia, Siberia, Eastern Russia, and Europe (Kawamura et al., 2012).

3. Results and Discussion

Anhydrosugars such as levoglucosan are ubiquitous in the atmosphere, which are emitted significantly from biomass burning activities and deposited on the ice crystals, and contribute to water-soluble organic carbon (WSOC) (Gennaro et al., 2015; Verma et al., 2015; Gao et al., 2015; Legrand et al., 2016; Grieman et al., 2017; Li et al., 2018; Grieman et al., 2018a,b; You et al., 2019). These are produced from the pyrolysis and combustion of cellulose and/or hemicellulose from wildfires and domestic wood fires at temperatures above 300 °C (Shafizadeh, 1984; Fraser and Lakshmanan, 2000; Simoneit et al., 2002) during the smoldering stage of a fire. Recently, Kuo et al. (2011) reported that levoglucosan and its isomers are produced at temperature up to 350°C. Many studies have shown that levoglucosan is the most

abundant anhydrous monosaccharide (Engling et al., 2006; Hoffmann et al., 2010; Kuo et al., 2011), which is tracked by other species of anhydromonosaccharides; e.g. mannosan, galactosan and/or dehydroabietic acid. Such specific characters and the sources can make levoglucosan a unique tracer (Simoneit et al., 1999; Jordan et al., 2006) in the southern Alaska as shown in Fig. 1.

In addition, historical trends of biomass burning tracers may represent the bulk effects of emissions, transport, transformations, and depositional and post-depositional process on the ice crystals (Grieman et al., 2017). Comparison of this study (e.g., concentration trends) with other ice core studies suggested that these compounds are well captured in the atmosphere and deposited to the ice sheets. Backward trajectories of this study and other ice core studies suggested common source regions (e.g., Russia, Siberia, and East Asia), from which it takes several days to reach the sampling sites (e.g., Greenland-Tunu, Svalbard, Akademii Nauk, and Aurora Peak of Alaska).

3.1 Levoglucosan

This study showed that average concentration of levoglucosan (range: BDL-20800, average: 543±2340 ng/kg-ice) is 8.6 times higher than that of dehydroabietic acid (range: BDL-556, ave. 62±97 ng/kg-ice) and 400 times higher than that of vanillic acid (range: BDL-18.6, ave. 1.5±2.9 ng/kg-ice) for 1665-2008 A.D. It should be noted that combustion of lignite (lignite includes fossilized cellulose) or hemicellulose emits levoglucosan and its isomers; e.g., mannosan and galactosan (Hoffmann et al., 2010; Kuo et al., 2011). However, we did not detect these isomer compounds (less than DL). In contrast, higher concentrations of these isomers and levoglucosan were reported in aerosol samples collected from the oceans via “round-

209 the-world cruise" (Fu et al., 2011), Mt. Tai in the North China Plain (Fu et al., 2008),
210 and urban tropical India (Fu et al., 2010) using the same method.

211 Levoglucosan may not be as stable as previously thought in the atmosphere
212 (Fraser and Lakshmanan, 2000; Hoffmann et al., 2010), however, its concentrations
213 are not seriously influenced during transport for several days (Fraser and Lakshmanan,
214 2000; Lai et al., 2014). Hence, we may speculate that levoglucosan could be stable
215 enough in the ice core studies. However, degradation of levoglucosan depends upon
216 the OH radical (Hennigan et al., 2010), which are automatically affected by relative
217 humidity of the atmosphere and air mass aging during long range atmospheric
218 transport from Japan, China, Mongolia, Siberia, and Russia to Aurora Peak.

219 Levoglucosan showed higher concentrations in around 1660s-1830s (Figure
220 2a) with sporadic peaks in 1678 (ice core depth: 174.6 m; concentration: 593 ng/kg-
221 ice), 1692 (172.2 m; 704), 1695 (170.3 m; 1250), 1716 (165.6 m; 990), 1750 (156.7
222 m; 913), 1764 (151.5 m; 1433), 1786 (147.3 m; 7057), 1794 (146.1 m; 3302) and
223 1834 (138.4m; 944) above its average concentration (542 ng/kg-ice). Source regions
224 of these higher spikes could be East Asia, Eastern Russia, Siberia, higher latitudes of
225 Alaskan regions, and Canadian regions. For instance, Ivanova et al. (2010) reported
226 the frequently occurred heavy forest fires (e.g., boreal forest) in spring, summer and
227 autumn in eastern Siberia in the past, which is a potential source region to Alaska.
228 This study showed higher concentrations of levoglucosan before the 1840s (Figure
229 2a). Marlon et al. (2008) further confirmed that there was intensive biomass burning
230 between the 1750s -1840s on a global scale, which is linked to increasing
231 anthropogenic activities (e.g., population growth and land-use change).

Similarly, we detected higher spikes of levoglucosan in 1898 (120.7 m; 577 ng/kg-ice), 1913 (114.8 m; 20800), 1966 (77.7 m; 692) and 2005 (13.7 m; 598) above the average concentration (542). Figure 2a clearly shows its lower levels than the average after the 1830s (except for 1898, 1913, 1966 and 2005 A.D.) compared to before 1830s. This decline could be attributed to less forest fire activity due to intensive grazing, agriculture, and forest fire management system (Marlon et al., 2008; Eichler et al., 2011). It should be noted that charcoal signals are scarce for Siberian regions compared to North American and European ice core records (Eichler et al., 2011). Moreover, two-third of Earth's boreal forest (17 million km^2) lies in Russia, which is a potential source of forest fires with a significant effect on a global air quality (Isaev et al., 2002; Eichler et al., 2011).

Ice core records of Mt. Logan from Canada, GISP2 and 20D (older than the 1850s) from Greenland are characterized by higher spikes of NH_4^+ superimposed with relatively uniform summertime and wintertime minimum (Whitlow et al., 1994). We obtained higher spikes of levoglucosan before the 1840s (Fig. 2a), which is consistent with higher spikes of NH_4^+ in 1770-1790 and 1810-1830 in the Mt. Logan data (e.g., Whitlow et al., 1994). This comparison suggests similar source regions of NH_4^+ for different sampling sites before the 1830s. In contrast, Mt. Logan data showed higher spikes of NH_4^+ in the intervals of 1850-1870 and 1930-1980, which is dissimilar (except for two points) to our results from Aurora Peak (Fig. 2a). It should be noted that Greenland ice core records (GISP2 and 20D) showed lower spikes of NH_4^+ compared to Mt. Logan (Whitlow et al., 1994) during these intervals (1850-1870 and 1930-1980). This is consistent with the results of Aurora Peak (except for 1966), again suggesting similar source regions (Holdsworth et al., 1992; Davidson et al., 1993; Whitlow et al., 1994). The potential source regions for Greenland ice cores

include northern North America, Europe, and Siberia, which are also likely source regions for Mt. Logan (Holdsworth et al., 1992; Davidson et al., 1993; Whitlow et al., 1994; Legrand et al., 2016). These regions may be associated with higher spikes in ice cores from Mt. Logan, Greenland and Aurora Peak of Alaska.

Except for a few points, e.g., 1999 (436 ng/kg-ice) and 2005 (598), concentrations of levoglucosan drastically decreased in 1980-2008. This decrease infers that forest fire activities could be depressed by many factors. For instance, Central and East Siberian forest fire activities were controlled by strong climate periodicity, e.g., Arctic Oscillation (AO), El Nino, intensification of the hydrological cycle in central Asia, and other human activities in the NH (Robock, 1991; Wallenius et al., 2005; Balzter et al., 2007; Achard et al., 2008; Eichler et al., 2011). Eichler et al. (2009) further confirmed that from 1816 to 2001 higher amounts of NH_4^+ and formate ($HCOO^-$) were directly emitted from biogenic sources rather than biomass burning (Olivier et al., 2006) in the Belukha glacier in the Siberian Altai Mountains. Moreover, lower concentrations of charcoal between 1700 and 2000 in this Altai Mountain further suggest that forest fire activities were weaker than anthropogenic activities in the source regions (Eichler et al., 2011).

Similarly, the sparsity of levoglucosan after the 1840s compared to the period of 1660s to 1840s means low intensity of biomass burning and/or significant deposition before reaching to the saddle of Aurora Peak, except for 1898, 1913, 1947 and 1966 A.D., which could be due to a point source around Alaskan region for levoglucosan rather than long-range atmospheric transport. For example, higher spikes of NH_4^+ at Mt. Logan during 1900-1990 A.D. are likely originated from central and eastern Siberia (Robock, 1991), which is dissimilar to the source regions in this study. The only exception is 1966 (2000 ng/kg-ice), suggesting that local biomass

282 burning and/or different source regions could be activated for levoglucosan is
283 important in southern Alaska during this period. Moreover, vanillic acid (VA) and p-
284 hydroxybenzoic acid (p-HBA) of Svalbard and Akademii Nauk (Eurasian Arctic) did
285 not show similar trends (Grieman et al., 2017, 2018a). It further suggests that central
286 and eastern Siberian regions did not contribute this compound significantly during
287 this period (1900-1990 A.D.) compared to other ice core studies (e.g., Fig. 6a-e)
288 and/or atmospheric circulations could be shifted.

289 The above results suggest the subsequent evidences: (a) heavy biomass
290 burning could be activated in the source regions, (b) short-range air mass circulation
291 could quickly reach southern Alaska, causing higher levels of levoglucosan; (c)
292 dilution and/or scavenging of biomass plume enroute could be maximized after 1830s,
293 whose mechanisms could be associated with dry and wet deposition, diffusion, and
294 degradation by hydroxyl radicals in the atmosphere during long range atmospheric
295 transport, (d) a common NH summertime biomass burning plume could be
296 significantly deposited during short-range atmospheric circulation on the exposed
297 surface area of the glaciers. Particulary, Mt. Logan, Svalbard, Tunu of Greenland and
298 Aurora have common source regions, e.g., Russia and/or Siberian forest as well North
299 America/Canadian forest (Figure 6a-e). These considerations support that Alaskan
300 glaciers can preserve most biomass burning events in the circumpolar regions, which
301 occurred in the source regions of Siberia, East Asia, Canada and Alaska.

302 Hence, these historical records of levoglucosan before the 1830s suggest that
303 long-range atmospheric transport was significant rather than short-range transport
304 from intense and widespread forest fires. For instance, forest fire intensity in 1660s-
305 1830s A.D. could be induced by lightning during drought seasons in the Siberian

regions as well as extensive burning to clear land for agriculture purposes in the NH (Whitlow et al., 1994; Legrand et al., 2016; Grieman et al., 2017; 2018a, b).

A declining trend in the concentrations of levoglucosan after the 1830s (except for few points) showed that sources could be changed significantly and/or forest fire activities could be suppressed and/or controlled in 1830s-1980s (Whitlow et al., 1994). It should be noted that 1400 A.D. to the end of the 1700s A.D. is the Little Ice Age (LIA) and after LIA to late 1800s is considered as the extended Little Ice Age (ELIA) (Mann et al., 2009; Divine et al., 2011;). This study shows that intense biomass burning activities (higher spikes) before the 1830s are somewhat similar to historical records of p-HBA and vanillic acid of Lomonosovfonna (Svalbard) and Akademii-Nauk ice core in the NH (Grieman et al., 2017, 2018a) except for some points (Fig. 6a,b,d). Hence, recent changes in the concentration trends in the Alaskan ice core are thought to be climate-driven. These climate-driven effects are further discussed in later section 3.4.

3.2 Dehydroabietic acid

Dehydroabietic acid is produced by pyrolytic dehydration of abietic acid from conifer resin. In other words, dehydroabietic acid is produced during the burning process of conifer resins (Simoneit et al., 1993; Kawamura et al., 2012;). It can be used as a specific biomass-burning tracer for conifer trees and other resin-containing softwoods in an ice core study. Dehydroabietic acid was detected as the second dominant species (range: BDL-556, ave. 62.4±97.2 ng/kg-ice), whose concentrations are 9 times lower than levoglucosan but more than 46 times higher than vanillic acid (range: BDL-18.6, ave. 1.62±2.96 ng/kg-ice). Dehydroabietic acid showed higher spikes in 1678 A.D. (ice core depth in meter, 173.9 m; 200 ng/kg-ice), 1716 (165.3 m;

67.5 ng/Kg-ice), 1728 (161.5 m; 139 ng/Kg-ice), 1732 (159.6 m; 233 ng/Kg-ice), 1738 (158.3 m; 113 ng/Kg-ice), 1750 (156.7 m; 66.9 ng/Kg-ice), 1764 (151.5 m; 331 ng/Kg-ice), 1786 (147.3 m; 386 ng/Kg-ice), 1794 (146.1 m; 78.6 ng/Kg-ice), 1913 (114.8 m; 101 ng/Kg-ice) than its average concentration (62.4 ng/kg-ice), and each consecutive years from 1994 to 2007 A.D. (depth range: 44.8-0.88 m) have concentrations of 92.8, 199, 141, 203, 136, 109, 98.5, 124, 124, 174, 309, 131, 298, and 555 ng/kg-ice. Vanillic acid from Svalbard (Grieman et al., 2018a) showed similar spikes with dehydroabietic acid in this study during the 1660s to 1790s A.D. In addition, Svalbard ice core showed relatively lower spikes from 1800s to 1980s as compared to 1660s-1790s A.D. In contrast, p-HBA in this study did not show a similar trend with Svalbard (Fig. 6a,b).

These periods are consistent with the higher spikes of levoglucosan, except for a few points (e.g., 1734-1738 A.D.) before 1990 A.D. (Fig. 2a, b). The historical trend of dehydroabietic acid is also similar to that of levoglucosan before 1980, which is consistent with Kamchatka ice core records (Kawamura et al., 2012). In contrast, Kamchatka ice core showed a gradual increase of dehydroabietic acid after the 1950s. However, we found an abrupt increase for dehydroabietic and vanillic acids in the Alaskan ice core after 1980 A.D. (Fig. 2b,c). These results suggest that biomass burning plumes of pine, larch, spruce and fir trees in Siberian regions have a substantial influence on Kamchatka, southeast Russia (facing to the western North Pacific Rim) than southern Alaska (facing to the eastern North Pacific Rim).

We found that concentrations of dehydroabietic acid in the Alaskan ice core after the 1980s were higher than those of levoglucosan, which is consistent with Kamchatka records (Kawamura et al., 2012). This further suggests that biomass burning plumes from Siberian boreal conifer trees could be transported to the North

355 Pacific regions including the eastern North Pacific Rim. It also suggests that East
356 Asian regions (broad-leaf trees are common) could be important for levoglucosan
357 rather than dehydroabietic acid (boreal forest fires in Siberia, where pine trees are
358 dominant). For instance, correlation of levoglucosan versus dehydroabietic and
359 vanillic acid from 1660 to 1840 are weak but significant (τ=0.37 and 0.33, $p<0.05$,
360 respectively), suggesting the presence of common source region. Correlation of
361 levoglucosan with dehydroabietic and vanillic acids from 1920 to 1977 are not
362 significant (0.11 and 0.14, respectively). On the other hand, vanillic vs.
363 dehydroabietic acid showed significant correlation (0.41, $p<0.01$), suggesting a
364 different source region for levoglucosan. Backward trajectories analysis (500 hPa) of
365 air masses (2002-2007 A.D.) together with fire counts also showed that sources
366 regions also include Mongolia, China and Japan (Fig. 7a-f). Yasunari and Yamazaki
367 (2009) reported that Alaska can receive air masses from East Asia and Japan in the
368 troposphere (>300 hPa). The Kamchatka Peninsula also can receive air masses from
369 these regions (Kawamura et al., 2012).

370 These results showed some similarity in the records of levoglucosan between
371 Kamchatka and Alaska ice cores (except for few points) and some discrepancies of
372 dehydroabietic acid between two sampling sites. Dehydroabietic acid concentrations
373 gradually increased in the Kamchatka ice core after the 1950s. Alaskan ice core
374 showed an increase after the 1970s (Fig. 6e), suggesting that conifer-burning plumes
375 could be transported significantly to Kamchatka as well, but not southern Alaska in
376 the 1950s-1980s. There is another possibility for this discrepancy between two sites,
377 i.e., dehydroabietic acid could be decomposed during long-range atmospheric
378 transport (Simoneit and Elias, 2001) from Siberia to southern Alaska although it could
379 easily reach to Kamchatka in the western North Pacific Rim. The Kamchatka ice core

also did not show high spikes (except 1970) in the 1950s-1970s. Such types of lower spikes and/or sporadic peaks of levoglucosan and dehydroabietic acid after the 1910s (Fig. 2a,b) and the correlations suggest that source regions should be different (e.g. East Asian broad leaf trees and Siberian boreal forest/pine trees), or regional transport overwhelms the long range atmospheric transport of dehydroabietic acid rather than levoglucosan over the saddle of Aurora Peak at least after the 1910s. Interestingly, dehydroabeitic acid showed an increasing trend from 1980s to onwards with higher concentrations than levoglucosan, being consistent with Kamchatka ice core (Kawamura et al., 2012).

Annual composite maps (Fig. 7a-f) of the Moderate Resolution Imaging Spectroradiometer (MODIS) from 2001 to 2007 show a continental outflow of air masses from Eurasia to the Aurora site, generally supporting the above results and implications for the Alaskan ice core. However, we detected higher spikes of levoglucosan (in 2004, 2005 and 2006 A.D. with 95, 598 and 131 ng/kg-ice, respectively), dehydroabietic acid (in 2004, 2006 and 2007 A.D. with 309, 298 and 556 ng/kg-ice, respectively) and vanillic acid (in 2005, 2006 and 2007 A.D. with 18.6, 7.30 and 12.7 ng/kg-ice, respectively) within these years, suggesting that they have different sources. It is well known that 2004 is the year of biomass burning in Alaska. The concentration of dehydrobaietic acid in 2004 (309 ng/kg-ice) is three times higher than levoglucosan (95.3 ng/kg, see Fig. 2), suggesting that boreal forest fires associated with conifer trees followed by short- and long-range atmospheric transport are more important in recent decades in the Northern Hemisphere.

3.3 Vanillic acid

403 We detected vanillic acid (VA) in the ice core from Aurora Peak (Fig. 2c),
404 which is a biomass-burning tracer of lignin (Simoneit et al., 1993). Particularly,
405 vanillic acid can be produced by incomplete combustion of conifer trees, i.e., conifer-
406 rich boreal forest (Simoneit et al., 1993; Pokhrel, 2015). We found that the levels of
407 vanillic acid are very low between 1830s and 1960s as shown in Figure 2c. Higher
408 spikes of a lignin tracer were detected in the following years: 1678 (3.25 ng/kg-ice),
409 1692 (3.23), 1695 (5.56), 1732 (3.98), 1786 (3.60), 1814 (11.0), 1818 (5.50), 1973
410 (5.52), 1989 (3.57), 1993 (2.66), 1996 (4.66), 1997 (3.5), 1999 (3.57), 2001 (3.26),
411 and 2007 (18.6). We found that the spikes of vanillic acid are not consistent with
412 those of levoglucosan in the ice core during the periods (Fig. 2). In particular, in more
413 recent years after 1990, vanillic acid showed a clear abrupt increase in the ice core,
414 which is consistent with the increase of dehydroabietic acid but different from
415 levoglucosan (Fig. 2). The abrupt increase of vanillic acid in the Alaskan ice core is
416 consistent with that of the Kamchatka ice core (Kawamura et al. 2012).

417 The higher concentrations and similarity of vanillic and dehydroabietic acids
418 in the Alaskan ice core after the 1990 suggests an enhanced emission of biomass
419 burning products of conifer trees and lignin in the boreal forests in Alaska, which
420 could be imprinted in the southern Alaska ice core. Interestingly, we found a
421 significant correlation (Fig. 3a) between dehydroabietic acid (except for 2005 A.D.)
422 and vanillic acid (τ=0.60, $p<0.01$) after 1990s, whose period corresponds to the Great
423 Pacific Climate Shift (GPCS, 1977-2007 A.D.). Being consistent with the warmer sea
424 surface temperature in the eastern North Pacific Rim during the GPCS periods (Meehl
425 et al., 2009), southern Alaska is influenced by the warmer temperature and dryness,
426 which triggered more chance of forest fires in the boreal forests, causing more
427 emissions of conifer and lignin tracers over the southern Alaskan atmosphere (Figs. 2

and 6). Interestingly, Kamchatka ice core also showed an increased concentration of these tracers after1970s (Kawamura et al., 2012).

Vanillic acid in the Alaskan ice core showed different trend from Svalbard ice core (Fig. 6e) after the GPCS (1976-77), suggesting different source regions. Dehydroabietic acid exhibits similar trend with p-hydroxybenzoic acid (p-HBA) of Svalbard ice core (Grieman et al., 2018a). p-HBA is produced from tundra grasses and peat species, suggesting a similar source of North Asia including Siberia. Its ice core record may be climate-driven in the North Pacific Rim. In contrast, the historical trend of vanillic acid from the 1770s to 1950s is similar to that (depressed trend) of Tunu Greenland ice core, except for few years of 1851, 1870, 1880, 1934, and 1946 (Fig. 6c), which infers that long range atmospheric transport from Russia may be a likely source. These two trends diverge markedly after the 1950s onwards. In addition, vanillic acid in this study exhibits a similar trend with p-HBA and vanillic acid in the ice core from Akademii Nauk (Grieman et al., 2017) in 1890s-1980s (Fig. 6d).

These results suggest that Alaskan glacier showed non-stationary multi-decadal variability of biomass burning tracers from tundra grasses and peat species. Notably, during the 1660s to 1820s, vanillic acid, dehydroabietic acid, and levoglucosan have higher spikes (Fig. 6a,b,c) at 4 to 9 points, which are common in other ice cores (Fig. 6a-d) in the NH. After these higher spikes, global (at least Tunu, Akademii Nauk and Aurora) depression of vanillic acid and p-HBA (1830s-1950) can be observed (e.g., Fig. 6a-d) in the NH, suggesting that similarity and variability of these acids are temporally and spatially heterogeneous in the NH under the climate driven forces. Historical trends of biomass burning tracers from this and other ice core studies, together with backward trajectories (Fig. 7a-f), suggest a common potential

source region of North Asia and North America, which are characterized by fire activities of boreal tundra woodlands, boreal conifer forests and peat.

Dehydroabietic acids and p-HBA may be unstable compared to photo-degradation of levoglucosan during long-range transport. For instance, a higher sensitivity of dehydroabietic acid was reported compared to levoglucosan (Simoneit and Elias, 2001; Simoneit et al., 2002). It should be noted that we did not detect p-HBA, which can be produced from incomplete combustion of grasses (Simoneit et al., 2002; Kawamura et al., 2012;) although showed p-HBA was detected in Kamchatka ice core (Kawamura et al., 2012). In contrast, we detected significant amounts of dehydroabietic acid from 1665-2007 in this study (Figure 2b). Hence, we may speculate that p-HBA could be unstable compared to levoglucosan, dehydroabietic acid and vanillic acid during long-range atmospheric transport.

Moreover, the historical trend of vanillic acid from 1800-2000 in Greenland ice core (McConnell et al., 2007) is entirely different from that of this study. Besides, the historical trend of vanillic acid shows many higher sporadic peaks during the Little Ice Age (LIA) and extended LIA (ELIA), which is somewhat similar to concentration trends of 10-year bin averages of p-HBA and vanillic acid from Svalbard ice core (Grieman et al., 2018a). These similarities could be due to a similar source and source regions. In contrast, dissimilarity of historical records of these compounds before and after ELIA suggests that shifting of atmospheric circulation or different spatial pattern of biomass burning and/or that climate-driven effects are deeply involved (Pokhrel et al., 2015). Hence these results further support a snap of biomass burning periodic cycles of Alpine glacier in the North Pacific Rim

3.4 Biomass burning tracers, temperature and climate: Atmospheric consequences

There is a direct relationship between the atmospheric temperature and pressure in the NH; that is, one variable (temperature/pressure) follows the same change when it comes to increasing and decreasing mode. This mechanism drives the atmospheric air mass from one place to another in the NH. For example, the semi-permanent Siberian High and Azores High drive the air mass from those regions to Alaskan (e.g., Aleutian Low) and Icelandic (e.g., winter air mass circulation) regions in the NH (Mantua and Hare, 2002). This Siberian High-pressure system (the vertical extent is up to 3 km from the surface) is one of the principal sources of polar air mass in the NH and is a principal factor to control air pollution in the Alaskan regions. Ten-day airmass backward trajectories (Fig. 7a-f) supported the same atmospheric transport pathways to southern Alaska. The consequences of such atmospheric circulation in the Alaskan region can be directly observed with the correlations of monthly (annual and seasonal) records of global lower troposphere temperature anomalies (GLTTA) with this study (Fig. 4a-o).

These pieces of evidence are further reflected by the Pacific Decadal Oscillation (PDO), which is characterized by relatively high temperature from the west to east coasts of the North Pacific Rim (Mantuna et al., 1997; Mantuna and Hare, 2002; MacDonald and Case, 2005; Shen et al., 2006). The similar trend of levoglucosan with five points running average of this PDO cycle, except for few points (e.g., 1750, 1834, 1870, 1913, 1934 and 1966) during the whole period of 1665 to 1995, represents ecological changes and/or changes in climate-driven biomass burning activities. These years, that is, 1750, 1834, 1870, 1913, 1934 and 1966 A.D., are influenced by micro and meso scale rather than synoptic and global scale weather

500 conditions and/or by long spikes represented by single fire events or seasonal biomass
501 burning activities (Fig. 5a,b). Hence, the positive/negative phase of PDO represents
502 zonal and/or meridional flows and elevated/depressed transport of levoglucosan to the
503 eastern North Pacific Rim.

504 In addition, winter precipitation (i.e., snowfall) is higher than usual in the
505 Alaskan coast. The annual precipitation of Aurora is increasing. The positive
506 correlations (R^2 or τ) of levoglucosan (except for few points, 1993, 1997, 1999 and
507 2005), dehydroabietic (except for, 1991 and 1998) and vanillic acids (except for 1998
508 and 2002) with winter temperature (GLTTA) are 0.55, 0.44 and 0.29, respectively,
509 after the Great Pacific Climate Shift (see Fig. 4-o). When the pressure decreases, the
510 temperature decreases, transporting air mass from higher (e.g., East Asia) to lower
511 pressure regions (Alaska). Similarly, we found further evidence of long-range
512 atmospheric transport due to a strong pressure gradient between Alaskan (e.g.,
513 Aleutian Low) and East Asian regions (e.g., Siberian high). For example, the
514 correlations (R^2 and τ) of these three compounds (except for a few points) are all
515 positive with seasonal (i.e., summer, autumn, and spring) and annual records of this
516 temperature (see Fig. 4a-o). In addition, the terrestrial plant derived biomarker such as
517 homologous serious of high molecular weight fatty acids ($C_{21:0}$ to $C_{30:0}$) showed
518 increasing trends after the GPCS from the same ice core. These acids are emitted to
519 the source regions by vaporization of leaf waxes during biomass burning processes
520 (Pokhrel et al., 2015). Hence, these tracers are associated with synoptic scale
521 radiative climate forcing (e.g., radiative lapse rate or temperature inversion) from the
522 surface to boundary layer. The down slope winds and drainage of wind in the Alaskan
523 regions may be associated with PDO and El Nino Southern Oscillation (ENSO) in
524 summer (MacDonald and Case, 2005; Shen et al., 2006).

525 The remarkable increasing trend of dehydroabietic acid (ave. 128 ng/kg-ice,
526 range: 6.59-555, SD ±126 and median 108.8) has occurred after the GPCS (1977-
527 2007 AD). We found a significant correlation (Fig. 3a) between dehydroabietic acid
528 (except for 2005) and vanillic acid (τ=0.60, $p<0.01$). In contrast, we found
529 insignificant correlations of levoglucosan with dehydroabietic acid (0.30) (except for
530 1981 and 1986) and vanillic acid (0.21) (except for, 1999 and 2005) after the GPCS,
531 that is, 1977-2007 A.D., revealing the local source emission. For example, the
532 biomass burning year of Alaska is 2004, which shows three times higher
533 concentrations of dehydroabietic acid (309 ng/kg-ice) than levoglucosan (95.3 ng/kg-
534 ice), suggesting that short range atmospheric transport enhances the dehydroabietic
535 acid under the local weather condition of Alaska.

536 The historical record of δD of the same ice core is well correlated with the
537 PDO cycle (Tsushima et al., 2015). Levoglucosan levels of this study are also allied
538 with periodicity of PDO (Fig. 5a,b) due to a Aleutian Low of North Pacific Ocean,
539 which is atmospheric air mass convergent near the southeast coast of Alaska (e.g.,
540 Aleutian Low represents the positive PDO). The average annual amplitude of δD
541 from this ice core is 30.9% (Tsushima et al., 2015). This high amplitude of δD could
542 not be conserved, if 100% of snow melting were occurred in the past. The coastal
543 record of climate change (e.g., winter storm development) of the Gulf of Alaska is
544 well correlated to the GPCS (1976 A.D.) in the PDO, suggesting that δD indicates the
545 air temperature of the saddle of the Aurora Peak.

546 The higher spikes of levoglucosan are similar to those of dehydroabietic and
547 vanillic acids from 1660s to 1970s. The positive/negative phases of both PDO
548 (MacDonald and Case, 2005; Trouet et al., 2009) cover all higher/lower spikes of

549 levoglucosan. The corresponding phase (positive/negative) of PDO varies from year
550 to several years and exhibits a tendency to cover historical intervals of these
551 compounds lasting several decades from 1660s to 1970s. The NAO's (wNAO) phase
552 are remain same for several years than PDO as shown in Figure (Fig. 5b). The
553 periodicity of NAO phase (positive/negative) does not represent the historical trends
554 (higher spikes/depression) of levoglucosan, dehydroabietic and vanillic acids (Fig. 5b,
555 c). This NAO represents atmospheric circulation between subtropical High and polar
556 Low (Trouet et al., 2009). In fact, NAO significantly dominates the North Atlantic
557 (e.g., North America) and European winter climate variabilities rather than those of
558 North Asia (i.e., Eurasia/Siberia), which is spontaneously inappropriate in this study.

559 **4. Summary and Conclusions**

560 This study has been conducted to better understand temporal trends of the
561 forest fire signals depend on the source region and proximity to the source and types
562 of vegetation in the source regions of southern Alaska since the 1660s A.D. Ice core
563 records of dehydroabietic acid, vanillic acid and levoglucosan showed predominant
564 multidecadal trends, suggesting the variations of fire regimes and the proximity to the
565 source, and changes in atmospheric circulation, land-use and/or ecological pattern in
566 the mid to high latitudes (≥ 30° N) at least before and after the 1830s and after the
567 Great Pacific Climate Shift (GPCS). Levoglucosan showed sporadic peaks during the
568 1660s-1830s, and single spikes in the 1898, 1913, 1966, and 2005 A.D. These spikes
569 indicate a significant contribution of biomass and/or biofuel burning attributing to
570 their source-specific emission and atmospheric stability in Alaskan regions.

571 Dehydroabietic and vanillic acids showed similar historical trends with
572 levoglucosan before the 1830s, suggesting that hard wood and conifer trees (e.g., resin

and lignin boreal conifer trees, deciduous trees and other higher plants) and perennial grasses (C_3 and C_4 plants) were simultaneously important as burning sources. The gradually increasing concentration trends of dehydroabietic and vanillic acids after the 1980s onward show a strong correlation (τ= 0.60, $p< 0.01$; after the GPCS; 1976), suggesting significant changes in either burning patterns (i.e., new land-use pattern or new ecological pattern) or atmospheric circulation over Alaska by the climate driven forces with exhibiting similar signals of biomass burning tracers compared to insignificant correlation of levoglucosan with these compounds.

The significant positive correlations (τ) of these three compounds with lower tropospheric global (annual and seasonal) temperature anomalies (GLTTA) suggest that Alaskan snow precipitation was involved with climate-driven forces at least after the GPCS to onwards. These tracers are allied with synoptic and global scale radiative climate forcing (e.g., radiative atmospheric lapse rate or inversion) from the surface to atmospheric boundary layer. The series of higher (lower) spikes of biomass burning tracers from Aurora Peak represent the positive (negative) phase of PDO periodicity cycles in the North Pacific Rim. The correlation of temperature and comparison with PDO cycle with this study are further covering the excellent signal of periodic cycle of climate-driven regime, that is, atmospheric activities, climate and weather conditions, ecological changes, and individual fire activities of source regions to the Aurora site.

The straight-forward historical trends of these three compounds were significant before the 1830s, which differ from the Kamchatka ice core record, suggesting that there are some differences between the western and eastern North Pacific Rim for the emission, frequency, and deposition. The concentrations of these

three compounds from Aurora Peak are higher than those from other ice core studies in the NH (e.g., Kamchatka, Svalbard, Tunu, and Akademii Nauk). In contrast, there are similarities of depressed concentration trend of Aurora with other ice core studies at least for one hundred years (e.g., 1890-1980s: Akademii Nauk, 1820-1960: Tunu Greenland), suggesting that sources of biomass burning tracers are further confined within the same regions, traveling from very long distances and are well captured within the snow particles. If it is true, these compounds might be involved as cloud condensation nuclei from the surface to 15.2 km, (i.e., cumulonimbus cloud), transporting thousands kilometers to Aurora. It bounds positive feedback for the climate change and/or climate variability in the North Pacific Rim.

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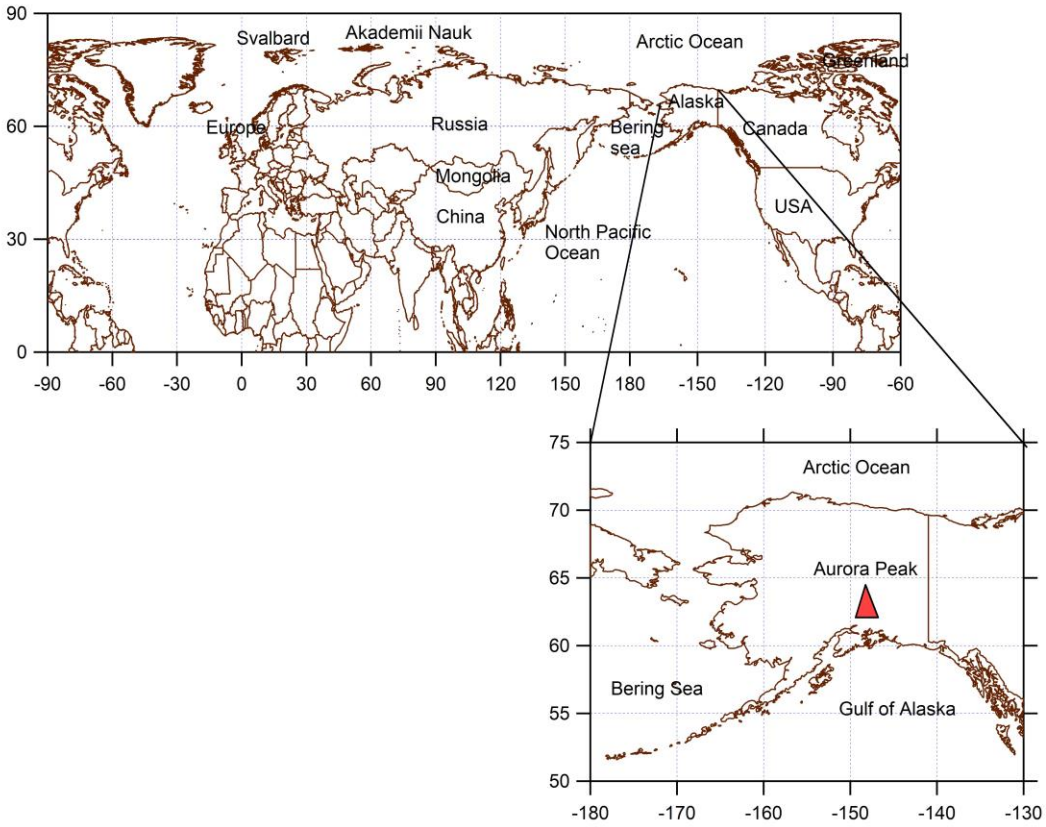
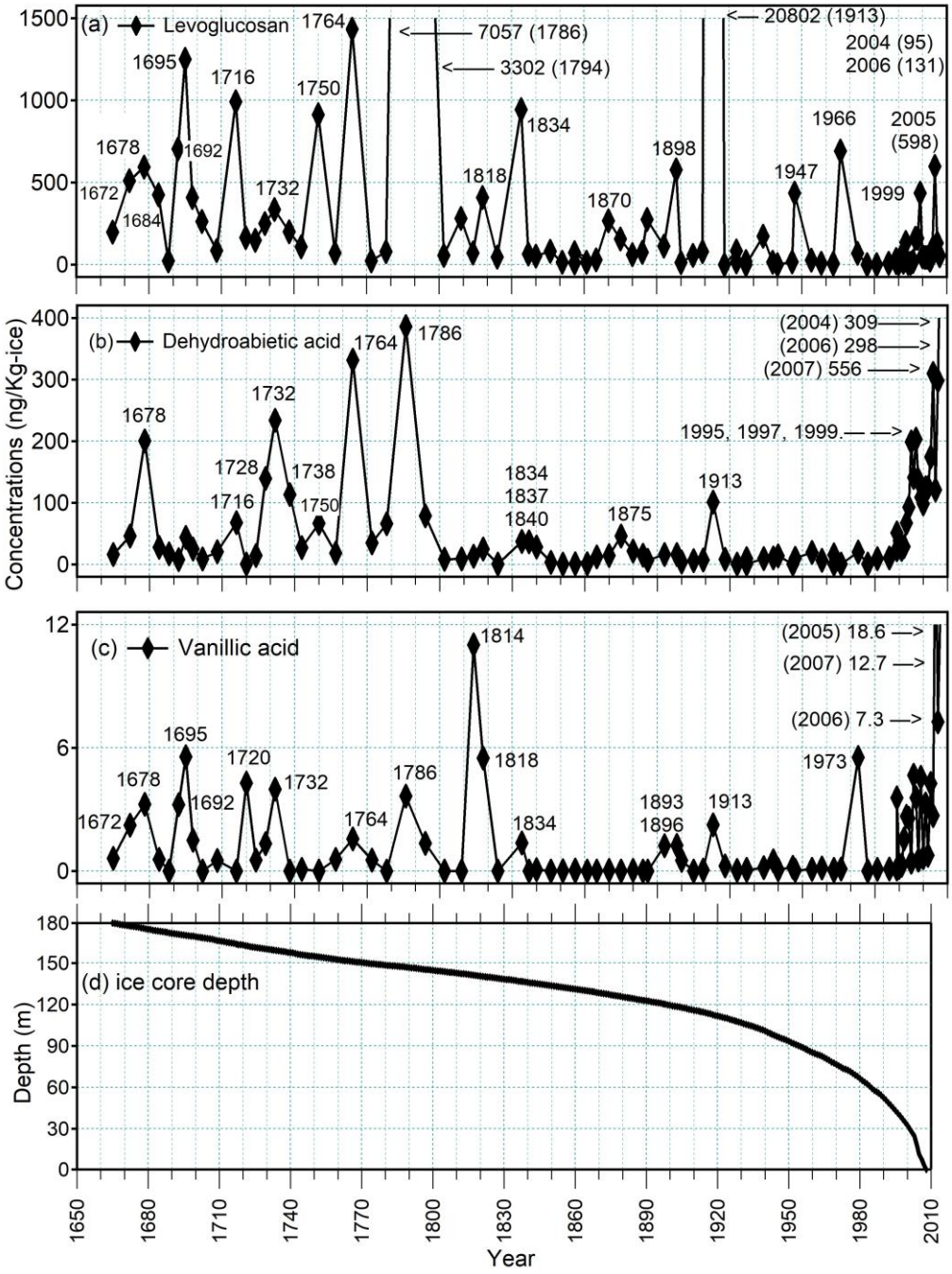


Figure 1. Geographical location of Aurora Peak in Alaska, where a 180-meter long ice core was drilled on the saddle of this peak in 2008



869

870 Figure 2. Concentration changes of (a) levoglucosan, (b) dehydroabietic, (c) vanillic
871 acids in the ice core, and (d) depth of the ice core collected from Aurora Peak in
872 Alaska for 1665-2008 A.D.

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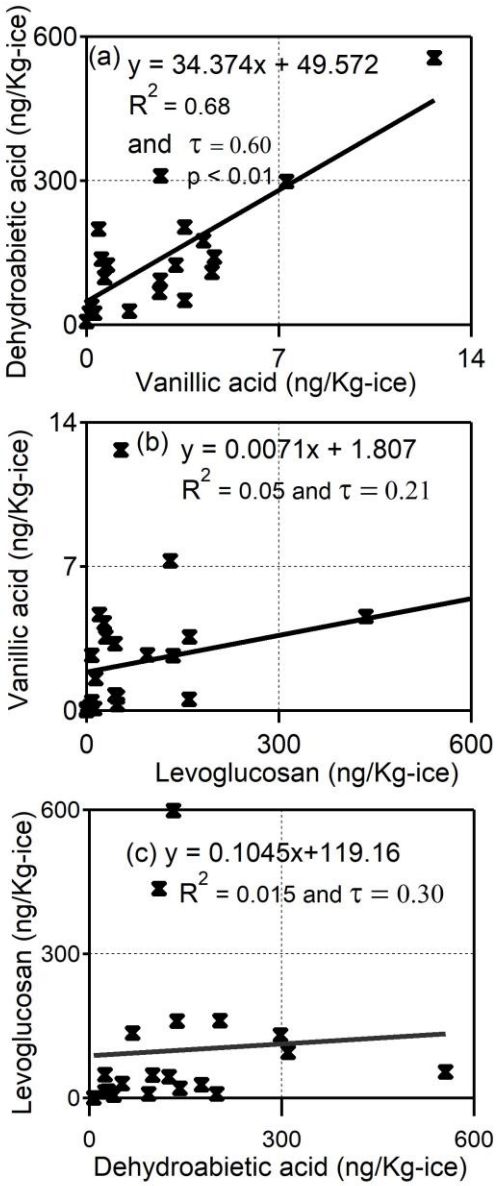

874

875 **Figure 3**. Correlations (Pearson: R^2 and Kendall: τ) plots between the concentrations
876 of (a) dehydroabietic and vanillic acids, (b) vanillic acid and levoglucosan, and (c)
877 levoglucosan and dehydroabietic acid. In (b) and (c), correlations are insignificant in
878 the Alaska ice core records from the saddle of Aurora Peak after the Great Pacific
879 Climate Shift (1977-2007 A.D.).

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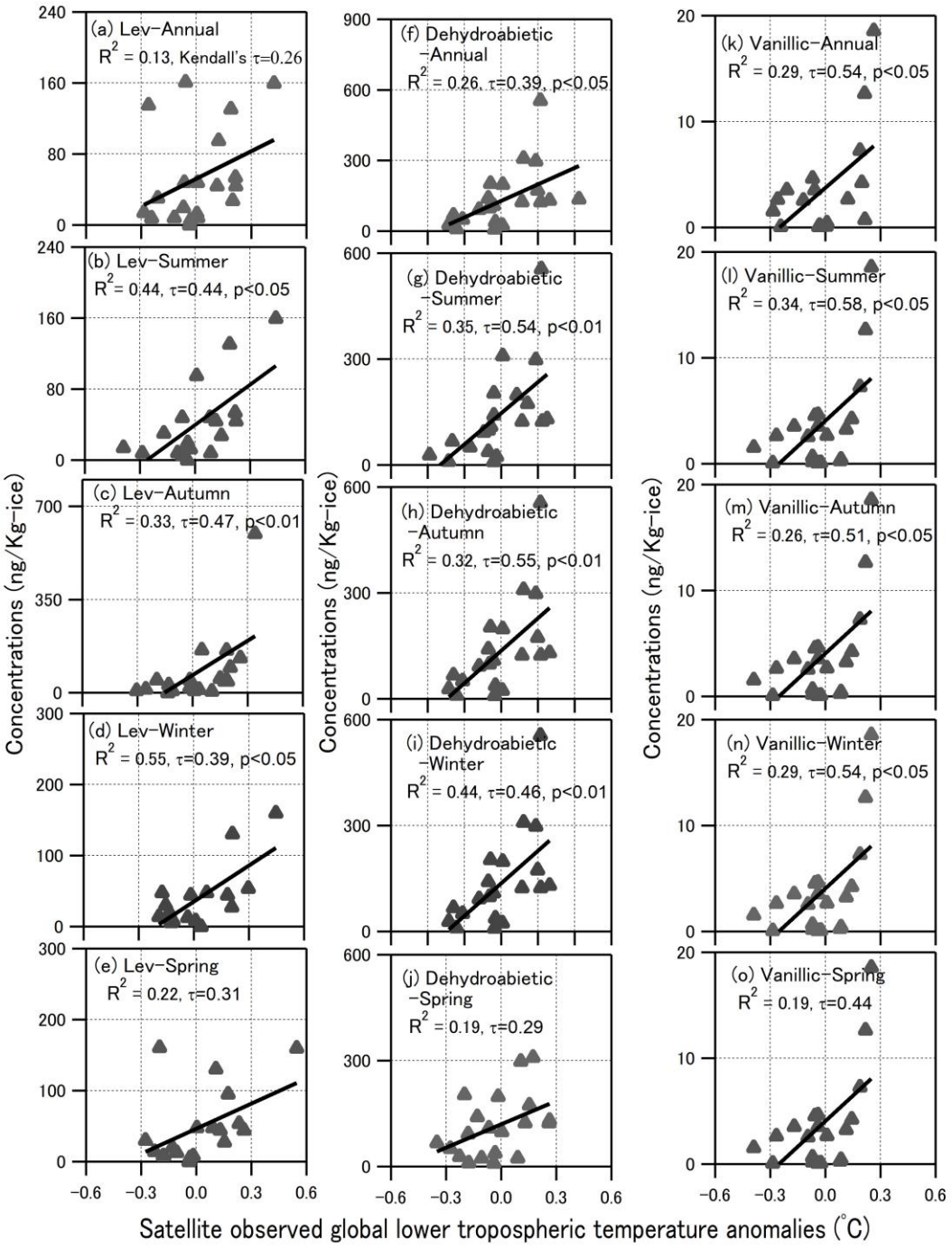

881

882 **Figure 4.** Correlation (Pearson: R^2 and Kendall: τ) plots between satellite-observed
883 global lower tropospheric temperature anomalies (i.e., microwave sounding unit
884 temperature anomalies (°C) of annual and seasonal records) and annual concentrations
885 of (a-e) levoglucosan, (f-j) dehydroabietic acid, and (k-o) vanillic acid after the Great
886 Pacific Climate Shift in the Northern Hemisphere.

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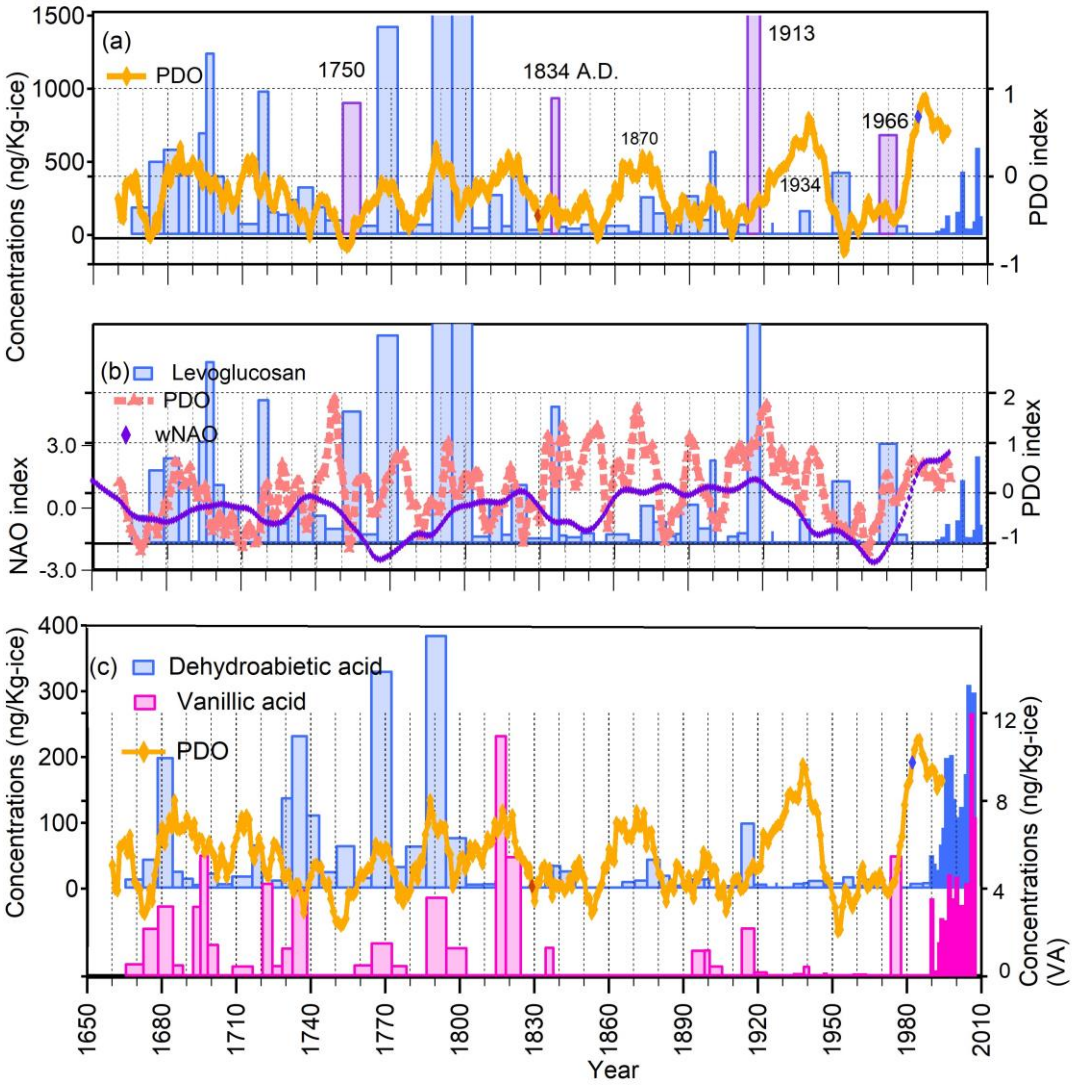

889

890 **Figure 5.** Historical trends in the concentrations of (a) levoglucosan (Aurora Peak) and
891 Pacific Decadal Oscillation (5 year mean PDO) index (Shen et al., 2006), (b) levoglucosan
892 (Aurora Peak), PDO-5 year mean index (MacDonal and Case, 2005) and Multi-decadal winter
893 North Atlantic index (wNAO) (Trouet et al., 2009), and (c) dehydroabietic and vanillic acids
894 and PDO for 1665-2008 A.D.

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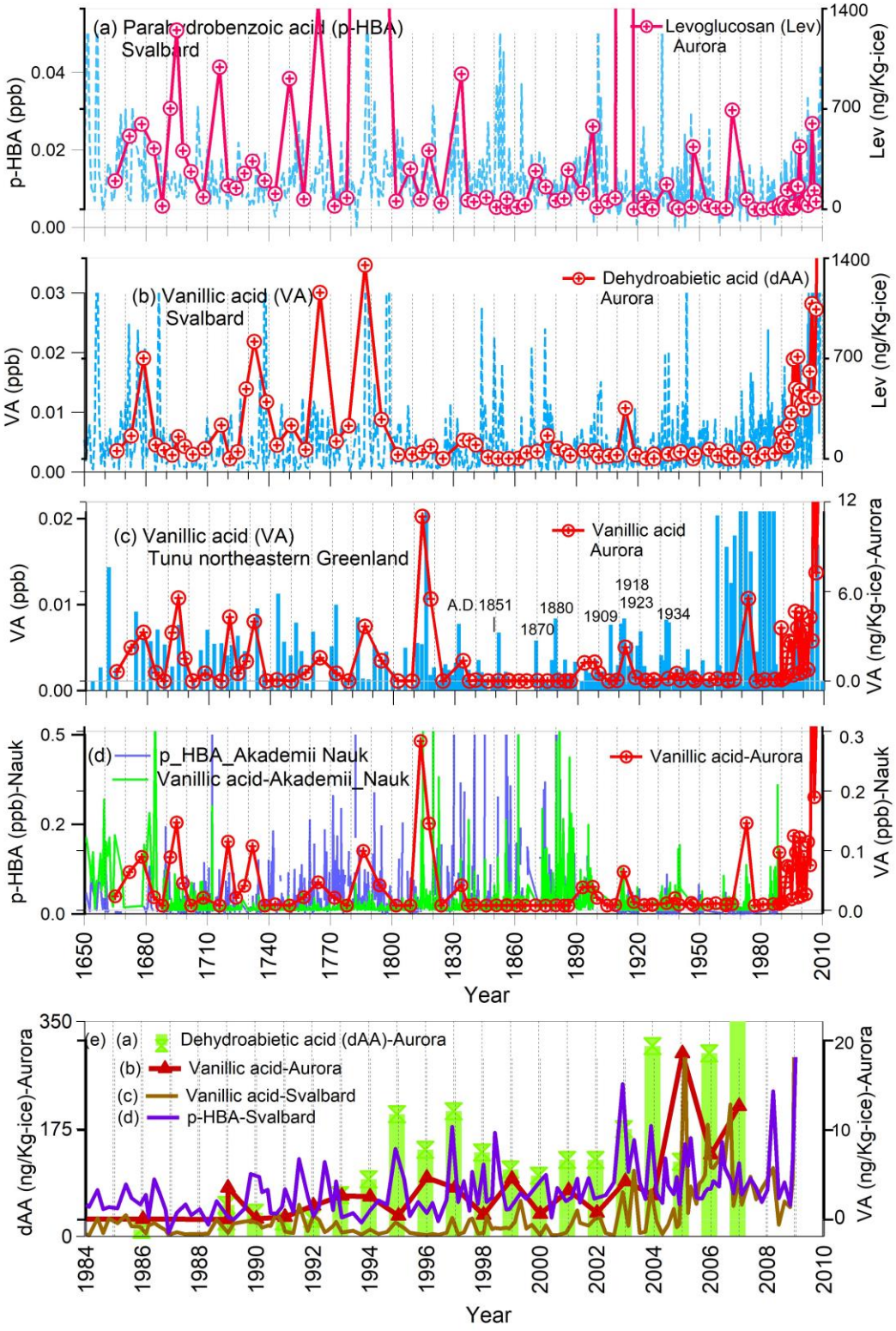

896

897 **Figure 6**. Historical trends of (a) p-hydrobenzoic acid (p-HBA) of Svalbard, (b) vanillic acid
898 (VA) of Svalbard, (c) VA of Tunu Greenland, (d) p-HBA and VA of Akademii Nauk, with
899 levoglucosan (Lev), dehydroabietic acid (dAA) and VA of Aurora Peak, respectively, and (e)

historical trends of dAA and VA of Aurora and VA and p-HBA of Svalbard after the Great Pacific Climate Shift (1977-2007 A.D.).

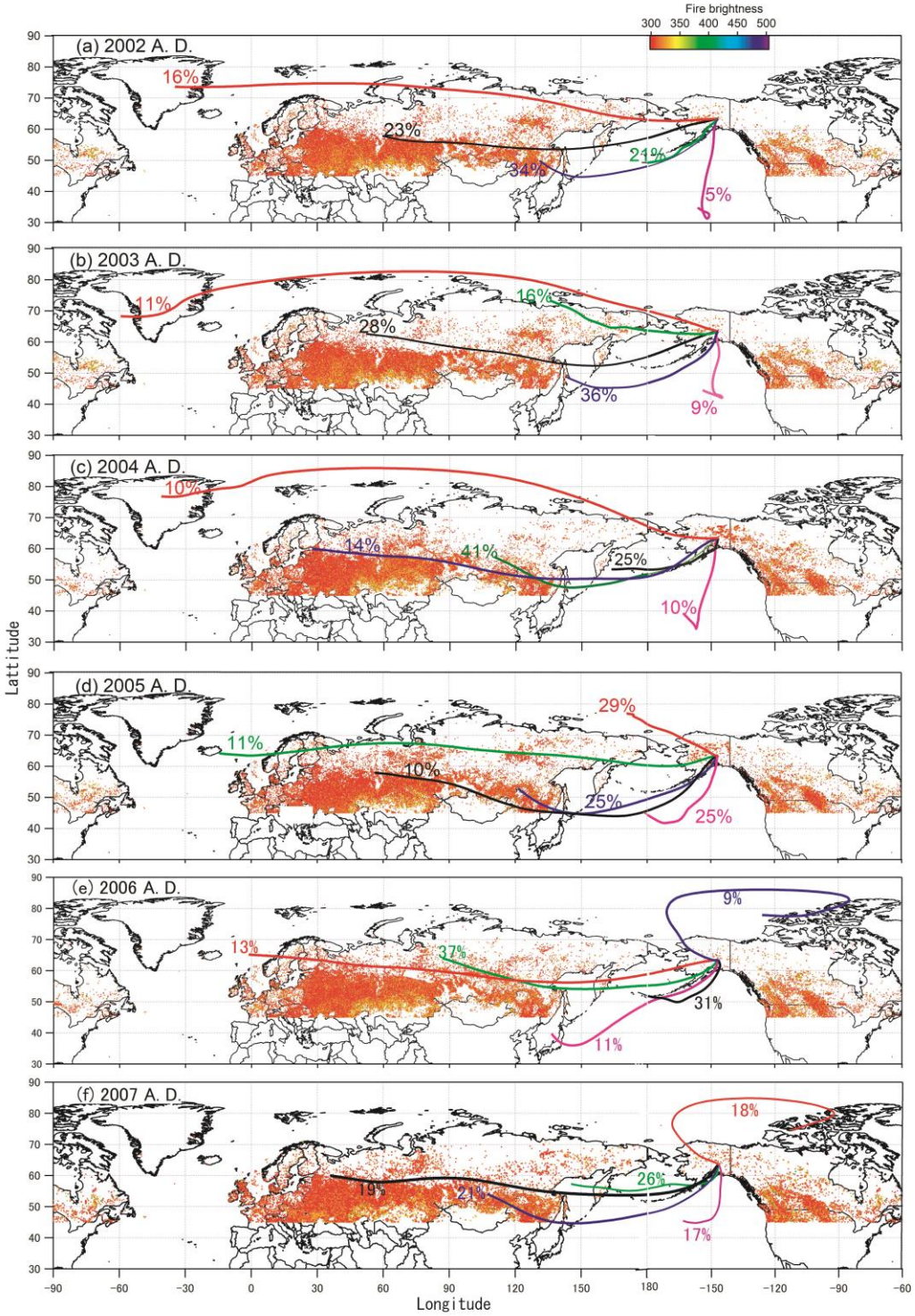

Figure 7. The MODIS fire spots together with 10 days back trajectories analysis (a-f) of Alaskan regions since 2001 to 2007.