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Climate of the Past Discussions

Interactive comment on "Aromatic acids in a Eurasian Arctic ice core: a 3000-year proxy record of biomass burning" *by* Mackenzie M. Grieman et al.

Mackenzie M. Grieman et al.

mgrieman@uci.edu

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The referee raised a few good points regarding the manuscript. These points are well taken and we appreciate the comments. The manuscript has been modified to take them into account. Referee comments are in italics and our responses are in a normal font.

Page 1, line 7: Could you provide the concentrations in [ng/l] as well (e.g.: 1 ppb=...ng/l)? I feel like [ng/l] is more widely used.

Revision: "The analyses were made using ion chromatography with electrospray mass spectrometric detection. The levels of these aromatic acids ranged from below the

detection limit (.01 to .05 ppb; 1 ppb = 0.001 ng/l) to about 1 ppb, with roughly 30% of the samples above the detection limit."

Page 1, line 10: "The timing of these periods coincides with the episodic pulsing of ice-rafted debris in the North Atlantic known as Bond events.". I would add "suggesting a link between fires and large-scale climate variability on millennial time scales"

Revision: "The timing of these periods coincides with the episodic pulsing of ice-rafted debris in the North Atlantic known as Bond events and a weakened Asian monsoon, suggesting a link between fires and large-scale climate variability on millennial time scales."

Page 2, line 25-26: I suggest you delete "because ammonium could be derived from these other sources", as you have already explained it a few lines above.

Revision: "Ice core proxies that are uniquely derived from burning are needed to confirm the interpretation of ammonium as a biomass burning tracer."

Page 2, line 27: I would add "... while it can also originate from fossil fuel combustion during industrial times".

Revision: "Black carbon in ice cores has been used as a tracer for preindustrial biomass burning (Chýlek et al., 1995; Legrand et al., 2016; McConnell et al., 2007; Rubino et al., 2015; Zennaro et al., 2014). During industrial times, black carbon in ice cores also originates from fossil fuel combustion."

The following reference has been added based in response to referee comment 4: Legrand, M., McConnell, J., Fischer, H.,Wolff, E.W., Preunkert, S., Arienzo, M., Chellman, N., Leuenberger, D., Maselli, O., Place, P., Sigl, M., Schüpbach, S., and Flannigan, M.: Boreal fire records in Northern Hemisphere ice cores: a review, Climate of the Past, 12, 2033–2059, doi:10.5194/cp-12-2033-2016, 2016.

Page 3, line 11: You could also mention dehydroabietic acid when citing burning of conifer.

Reply: It is true that dehydroabietic acid is produced, but here we were describing production only of the acids analyzed in this study, rather than the wide range of compounds produced from conifer combustion.

Page 3, line 16-17: In the Introduction, you have discussed the effects of emissions, transport and transformations, but I feel that you should discuss depositional and post-depositional processes more in details. What do we know about possible postdepositional processes?

Add to end of paragraph: "...Near surface postdepositional processes such as revolatilization, photochemical reactivity, or melt-water infiltration have not been studied for aromatic acids. Such processes could potentially influence the ice core levels of these compounds, particularly at low accumulation sites (Grannas et al., 2007)."

Also p8, line 5, replace with: "Given the absence of indication of any postdeposition artifacts, we interpret ice core VA and p-HBA as tracers for biomass burning variability. Further investigation of such effects is warranted, particularly for low accumulation ice core sites."

Page 3 line 27: I suggest you call them "back-trajectories".

These were forward trajectories in the study referenced. The following clarification was made:

Revision: "FLEXPART model forward trajectories suggest that in the summer aerosol transport to the Arctic from biomass burning sources is primarily from Siberia (48°-66°N, 60°-140°E; Stohl, 2006). The FLEXPART model is a Lagrangian transport and dispersion model that is used to simulate long-range atmospheric transport. Twenty-five percent of FLEXPART modelled forward trajectories from Siberia reached the Arctic in 3 days, and 50% reached the Arctic in 10 days (Stohl, 2006)."

Page 4, line 24-25: Are there blanks to test any possible contamination from the melter?

Reply: Melter blanks for VA and p-HBA gave medians of 0.0093 ppb (n = 75) and 0.025 (n = 56), excluding outliers (> 2 times the standard deviations), which are below the limits of detection.

Page 4, line 28-30: Why did you decide to opt for this second ice age scale? Do you consider it more accurate? If so, why? How older do you mean when you say "substantially older"? Please, provide numbers.

The preliminary age scale for the lower part of the ice core (Fritzsche et al., 2010) was originally based on geophysical flow modeling, but unconstrained by chemical correlations. High resolution, continuous flow analysis of multiple elements provided improved dating via identification of volcanic peaks and correlation to other ice cores.

The manuscript was changed as follows:

The original chronology for the upper 411 m of the core (900-1998 CE) was developed based on annual layer counting of stable water isotopes and volcanic sulfate signals (Opel et al., 2013). A preliminary chronology for the lower part of the ice core (i.e. below 411m) was developed based on an adjusted Nye geophysical flow model (Fritzsche et al., 2010) but unconstrained by chemical correlations. Therefore, an alternative age model was developed and used for this study (Fig. S2). This age model is based on correlation between high resolution multi-element continuous flow measurements of the Akademii Nauk ice core and other Arctic ice cores (Sigl et al., 2013). This new age scale yields older ages for the lower part of the ice core (below 411 m). The new age scale yields an age of 1100 BCE at 661 m as compared to 694 m for the preliminary age scale.

Page 6, line 4: A subset of how many samples were analysed using HPLCESI/MS/MS?

Revision: "In addition, a subset of 1,074 Akademii Nauk samples were analysed as replicates for vanillic acid using the older HPLC-ESI/MS/MS method described by Grieman et al. (2015)."

Page 6, line 26: "We are not aware of any laboratory combustion studies of the larch typically comprising the likely source regions". This sentence is not clear to me. What do you exactly mean?

Revision: "Laboratory studies of biomass burning indicate that syringic acid is not a component of burning-derived aerosols from conifers (Iinuma et al., 2007; Otto et al., 2006; Rogge et al., 1998; Simoneit et al., 1999). We are not aware of any laboratory combustion studies of plant species typical of Siberian forests or tundra."

Page 6, line 29: From figure 3, I would not say that the levels of VA are generally higher than those of p-HBA in the PILH. Could you specify how you have compared the levels of the two molecules (average, maxima, ...) and possibly provide the numbers for them?

Revision: "Throughout the preindustrial Late Holocene (prior to 1700 CE), the levels of VA generally are higher than those of p-HBA. The median and mean of the ratio of VA to p-HBA prior to 1700 CE were 1.4 and 4.4, respectively."

Page 7, line 3-4: How did you quantify the percentage of melt layer in figure S4? Is this already published data?

The melt-layer data have not been published. The following melt-layer percentage definition has been added to the caption of figure S4:

Revision: "Melt layer percentage is defined as the amount of melt-layer ice in each meter of ice by weight (Fritzsche et al., 2005)."

Page 7, line 7: I would like you to give a definition of the LOESS smoothing either in the Methods section or here.

Revision: "To remove short-term variability, smoothed records were constructed using log-transformed 40-year bin averaged VA and p-HBA records. The exponentials of the smoothed log-transformed records were used to present the records in concentration units (Fig. 4). Smoothing was also carried out using locally weighted polynomial

regression (LOESS; Cleveland and Devlin, 1988). Bin-averaged and LOESS smoothing of the Akademii Nauk organic acid records show essentially the same centennial to millennial-scale features that are clearly visible in the raw data (Fig. S5). As evident from visual inspection of the bin-averaged record, VA and p-HBA are correlated (r^2=0.47, p <10-6, n=80; Fig. 5)."

Revision: Fig. 4 and Fig. 5 have been reordered.

Revision: "For the purposes of this study, we define elevated periods as including data for which the standard error bands for 40-year binned averages reach or exceed the upper quartile of the entire dataset (Fig. 4).

The following reference was added: Cleveland, William S.; Devlin, Susan J. (1988). "Locally-Weighted Regression: An Approach to Regression Analysis by Local Fitting". Journal of the American Statistical Association. 83 (403): 596–610. doi:10.2307/2289282

FigS5 caption revision: "LOESS is a smoothing method using locally weighted polynomial regression (LOESS; Cleveland and Devlin, 1988)."

Page 7, line 14: I would write the periods here

Revision: "Three periods of elevated VA are identified (1180-660 BCE, 380-660 CE, and 1460-1660 CE), all of which are shared by p-HBA."

Page 7, line 23: Together with the period 180-220 CE?

Revision: "Periods of elevated p-HBA levels are identified from 180-220 CE and 1780-1860 CE, using 40-year bin averaging of the entire dataset. These periods are qualitatively different from the other elevated intervals in that p-HBA is more abundant than VA."

Page 7, line 30: If recent VA and p-HBA observations in Arctic snow and atmosphere were available, you could go one step further and use first-order assumptions on trans-

port, transformations and post-depositional processes to estimate the atmospheric aerosol concentration of VA and p-HBA in the region of the Nauk ice core and in the source region, similarly to what done by Fischer et al. (2015) for ammonium. I don't know whether recent VA and p-HBA observations are available, but you might want to cite Fischer et al. (2015) anyway, saying that it provides a method to estimate atmospheric concentrations in the source regions, provided that recent observations are available.

This suggestion is a promising approach for how to compare measurements of VA and p-HBA from several ice core sites, as is done in Fischer et al. (2015), in a future study. The following was added to this paragraph:

"However, large volcanic sulfate peaks throughout the record do not exhibit evidence of loss of aromatic acids. In this study, the VA and p-HBA are interpreted as tracers for biomass burning variability. Future studies should examine the relationship between levels of aromatic acids in air and snow, in order to develop transfer functions following the method of Fischer et al. (2015)."

Page 8, line 12-16: There is an assumption here that you should discuss: atmospheric circulation has not changed over the past 3000 years. How likely is that assumption to be valid? Is there no evidence of changes of atmospheric circulation over the last millennia, especially over climatically relevant periods, such as the Medieval Climate Anomaly and the Little Ice Age? Some discussion is needed.

Revision added to this paragraph: "The possible source locations for biomass burning impacting the Akademii Nauk ice core site were identified by calculating the fraction of air mass back trajectories from the ice core site originating in or passing over Siberia (defined as east of 42°E), Europe (defined as west of 42°E), or North America. This analysis assumes present-day meteorological conditions. Changes in atmospheric circulation patterns over the past millennia may have occurred, but are not considered here."

Page 10, line 4: I guess you do not mention anthropogenic influence on biomass burning because the human presence in Siberia is negligible. If so, I would spell it out, stating that the lack of significant anthropogenic activity allows you to interpret variations in biomass burning proxies and climate with a cause-effect relationship.

The following has been added prior to this paragraph: "Variability in biomass burning can be caused by human activity. The effect of humans on Siberian wildfire activity is not well-established. Human civilizations were predominantly nomadic in Siberia prior to 16th century. Comparison between pollen records, civilization development, and climate in the Lake Baikal region suggests that vegetation changes were more likely linked to climate than human-induced land use change throughout the Holocene (Tarasov et al., 2007)."

Page 10, line 5-7: See also Seki et al. (2015), Scientific Report

This reference has been added.

Page 10: line 32: I would add "Figure 8, bottom plot"

Revision: "Simultaneous changes in climate also are observed in the Chinese speleothem record from Dongge Cave, centered at: 2,700, 1,600, and 500 years before present (750 BCE, 350 CE, and 1450 CE; Fig. 8, bottom plot; Wang et al., 2005)."

Supplementary Figure S1: What do red lines/letters mean? Do they refer to the typical fragmentation in the Mass Spectrometer, as explained at page 5, line 22 of the main text? I would add some explanation in the figure's caption.

The red lines were meant to indicate the functional groups. They complicated the figure unnecessarily and have been removed.

Technical comments:

Page 2, line 3: replace "difference" with "different"

Revision: "These records cover very different age ranges at varied temporal resolu-

tions."

Page 6, line 23: replace "gasses" with "grasses"

Revision: "Syringic acid is structurally related to the lignin commonly found in grasses, including tundra grasses, and its absence in the ice core may simply indicate that grasses were not a significant component of the parent fuels (Oros et al., 2006)."

Page 9, line 19: there is a comma missing between p-HBA and VA: "In that study, elevated p-HBA VA,.."

Revision: "In that study, elevated p-HBA, VA, dehydroabietic acid, and levoglucosan were observed during the periods from 1700-1800 and 1880-2000 CE."

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