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Climate of the Past Discussions

Interactive comment on "A method for analysis of vanillic acid in polar ice cores" *by* M. M. Grieman et al.

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Response to reviewer comment: C1117 by Michel Legrand

Dr. Legrand raised two issues regarding the manuscript. Both of the points are well taken and we appreciate the comments. The manuscript has been modified to take them into account.

Issue 1. Introduction

"In the introduction, you wrote 'Ammonium, potassium, acetate, nitrate, oxalate, lev-

oglucosan, and black carbon in ice cores have also been used as proxies for biomass burning emissions (Whitlow et al., 1994; McConnell et al., 2007; Gambaro et al., 2008; Kehrwald et al., 2012). Of these proxies, only levoglucosan is exclusively due to biomass burning.' These statements are not totally correct, some key references are missed, and need to be modified. . .."

We have modified the introduction as follows:

"Past fire events have been detected in Greenland ice from enrichment of ammonium formate and oxalate, and the transport of these chemicals to Summit, Greenland in biomass burning plumes has been documented (Legrand et al., 1992; Dibb et al., 1996; Jaffrezo et al., 1998; Savarino and Legrand, 1998). Acetate and formate also have biogenic sources, which may limit their utility as fire proxies at less remote, continental ice core sites. In a continental Siberian ice core, a fire history was reconstructed from charcoal particles and variations in potassium and nitrate (Eichler et al., 2011). Another ice core chemical used as a biomass burning tracer is levoglucosan, an aerosol-borne anhydrous sugar exclusively produced by burning of cellulose. Levoglucosan is generated from combustion of all types of cellulose-containing plant matter, and is therefore not specific to a particular plant type or ecosystem (Simoneit et al., 1999). Levoglucosan has been detected in air over Summit, Greenland, and in both Greenland and Antarctic ice (Kehrwald et al., 2012; Gambaro et al., 2008; Zennaro et al., 2014). There has been some debate about the atmospheric reactivity of levoglucosan, and its suitability as a quantitative tracer for aerosol source apportionment (Hoffmann et al., 2010; Hennigan et al., 2010; Slade and Knopf, 2013)."

Issue 2: Conclusion

"In your conclusion when comparing your method to the one from Kawamura et al. (2012), I suggest to add the following sentence:

"Though the GC-MS method permits also measurements in the same sample of levoglucosan, p-hydroxybenzoic and dehydroabietic acids that are also of interest for

biomass burning ice record, the required small samples of our method permit to document with temporal high resolution these sporadic biomass burning events in view to study inter-decadal magnitude and frequency of events in relation with past climate, for instance."

This is a good point. We revised the concluding paragraph (page 2812, line 7) as follows:

"The detection limit achieved in this study was sufficiently sensitive to detect vanillic acid in a Siberian ice core. The GC-MS method has a lower detection limit (5 ppt, Kawamura et al., 2012) and permits simultaneous measurements of a wide range of additional organic compounds derived from biomass burning. However, that technique requires large samples (80–250 mL) and more extensive sample handling. The very small sample size and reduced sample handling requirements of the LC-ESI-MS/MS method makes it useful for analyzing ice cores at high temporal resolution, which is needed in order to study variability in fire magnitude and frequency on decadal time scales. The potential exists to extend the LC-ESI-MS/MS technique to measure to additional biomass burning products, as has been done for aerosols (Zangrando et al., 2013). This will be a focus of future work."

The following references were included in the manuscript:

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Eichler, A., Tinner, W., Brusch, S., Olivier, S., Papina, T., and Schwikowski, M.: An ice-core based history of Siberian forest fires since AD 1250, Quat. Sci. Rev., 30, 1027-1034, 10.1016/j.quascirev.2011.02.007, 2011.

Legrand, M., De Angelis, M., Staffelbach, T., Neftel, A., and Stauffer, B.: Large perturbation of ammonium and organic acids content in the Summit-Greenland ice core -

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Interactive comment on Clim. Past Discuss., 10, 2805, 2014.