Review by Michel LEGRAND of the manuscript entitled “A method for analysis of vanillic acid in polar ice cores” by Grieman, Greaves, and Saltzman.

This paper reports on a method that was developed to analyse vanillic acid in melted polar ice core samples. Vanillic acid is here chromatographically separated using reversed phase LC and detected using electrospray triple quadrupole mass spectrometry (ESI- MS/MS). Using a 100µL volume sample (with an analysis time of 4 min), a detection limit of 58 pptw is reached. The method is successfully tested on Arctic ice core samples from the Siberian Akademii Nauk. Vanillic acid is a product of conifer lignin combustion, which among a wide variety of organic species produced in biomass burning processes, is archived in polar ices. Given the important role played by biomass burning on either the climate or the key biogeochemical cycles of C or N, reconstructing its past history is of great interest for the community of atmospheric chemists and climatologists. The present contribution proposing a fast and not too much ice consuming method to analyse vanillic acid is thus welcome to the journal Climate of the past.

The paper is well organized, clearly written and concise. I only have two points for which I propose corrections of the manuscript:

In the introduction, you wrote “Ammonium, potassium, acetate, nitrate, oxalate, levoglucosan, 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.

First, it was previously clearly stated that potassium is far less useful than other species to trace back biomass burning due to marine and terrestrial sources, even if corrected to remove these contributions (e.g. non-sea-salt and non-crustal K+) (see Legrand and De Angelis, 1996; Savarino and Legrand, 1998). Second, while an acetate perturbation is often detected along biomass burning events recorded in Greenland ice layers, Legrand and De Angelis (1996) found that, in relation with post-depositional effects, the acetate perturbation is more difficult to detect because of a wider peak around the main biomass burning snow layers. Third, it was very clear that nitrate is found to be disturbed in some events (not all) and thus is not a good proxy of forest fires in Greenland ice (see Savarino and Legrand, 1998). Fourth, it was also obvious that, as discussed by McConnell et al. (2007), black carbon originates both in biomass and fossil fuel burning.

I therefore propose the following statements:

“Examining forest fires in ice cores started with the pioneering work of Legrand et al. (1992), which identified an input of ammonium and formate with a molar ratio close to unit and of oxalate in Greenland ice layers corresponding to forest fire events. This was confirmed by Dibb et al. (1996) and Jaffrezo et al. (1998) who reported a sudden increase of the atmospheric levels of these species at Summit (central Greenland) in August 1994 and June 1993 when biomass burning plumes were transported to the site from the northern Canada. Finally, Kehrwald et al. (2012) showed that the Summit snow layer corresponding to the August 1994 event exhibits oxalate and levoglucosan concentration peaks.

While NH_4COOH and $C_2O_4^{2-}$ are useful to detect biomass burning events reaching the remote Greenland ice cap, such an approach becomes less straightforward when working on ice cores extracted at less remote sites. For instance, the use of ammonium or formate, was less straightforward to extract the frequency of fires in an ice core from Altai (Siberia) due to large biogenic emissions around (Eichler et al., 2011). That motivated the development of methods to measure other proxies such as levoglucosan that are exclusively due to biomass burning."

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

The detection limit of 58 pptw achieved in this study using LC-ESI-MS/MS was sufficiently sensitive to detect vanillic acid in the Siberian ice core samples analyzed. The GC-MS method commonly used for aerosol analyses has a lower detection limit (5 pptw, Kawamura et al., 2012), but this method requires large samples (80–250 mL) and more extensive sample handling. 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.

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