

## ***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 by Referee 3

Referee 3 raised several issues regarding the manuscript. These points are well taken and we appreciate the comments. The manuscript has been modified to take them into account.

Issue 1. Introduction

“one important reference is missing (Zangrando et al., 2013) in which HPLC-MS/MS

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analysis is used to quantify vanillic acid (together with other biomass burning tracers) in arctic aerosol. . .”

That reference is very relevant and has been added to the introduction, as follows:

. . . Zangrando et al. (2013) reported detection vanillic acid and other phenolic compounds in Arctic aerosol samples using high performance liquid chromatography with tandem mass spectrometric detection (HPLC/ESI-MS/MS), which avoids the need for chemical derivatization prior to analysis.”

Issue 2.

“Why wasn’t any attempt made to include other biomass burning tracers in this study as well?”

We did attempt analysis of several other biomass burning tracers but were unsuccessful for a variety of reasons. It is certainly possible in principle to extend this approach to other compounds (as Zangrando et al., 2013 did for aerosol analysis), but further work would be necessary in order to demonstrate this.

Issue 3. 2 Instrumentation and 3.2 chromatography

“Section ‘2 Instrumentation’ and ‘3.2 Chromatography’ present some redundancies. I suggest merging the two sections.”

The following sentence inadvertently appeared in both sections. It has been removed from “2 Instrumentation:”

“The LC was operated isocratically using a mobile phase of 25 % methanol in water flowing at 200  $\mu\text{L min}^{-1}$ , a C18 reversed phase analytical column, and a 100  $\mu\text{L}$  injection loop.”

Issue 4. Page 2810, line 10-12.

“I find the calculation of the LOD not very robust and somewhat unconventional. Often

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LOD is calculated as 3 times the standard deviation of the blank (Gambaro et al., 2008) or following IUPAC recommendation (Currie, 1999)."

The LOD is now defined as 3 times the standard deviation of the blank, and the text revised to read:

"The detection limit is approximately .077 ppb, defined as three times the standard deviation of vanillic acid levels in distilled water blanks spiked with internal standard."

Issue 5. 3 Method Optimization

"Although ice cores samples are very clean I think that the accuracy of the method should be tested with matrix-matched standards or samples spiked with known amounts of vanillic acid."

The use of isotope-labeled standards is a rigorous way of assessing matrix effects. The response of the isotope was the same in ice core standards as in standards, indicating that matrix effects were negligible.

We modified the paragraph at line 10 of p2811 as follows:

"The rationale for using stable isotope-labeled internal standards in this study was to account for potential matrix effects that might suppress or enhance analyte response in an ice core sample compared to that in a pure water standard. The response to the isotope-labeled standard in ice core samples was identical to that in standards prepared in pure water. This indicates the absence of significant matrix effects in the Akademii Nauk samples."

Issue 6. Page 2811, lines 8-9

"Were the samples analysed always in duplicates but only 5 were above LOD? It would be nice to expand this to more samples and include a figure in which the precision is plotted against concentration levels of real samples."

The following will be added to the "4 Ice core analysis" section:

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"The relative standard deviation of duplicates is about 30% for levels above the LOD and below 0.6 ppb (n= 167)."

The following figure will also be added.

Figure 4. Measured vanillic acid level (ppb) compared to replicate vanillic acid level (ppb) (top). The line is the least squares fit accounting for both the original and replicate measurements. Vanillic acid level (ppb) compared to the relative deviation (%) (bottom).

Issue 7. Page 2811, line 12-15

"In ice core analysis, the presence of strong acids or bases (nitrate, sulfate, ammonia, etc.) could be the source of matrix effects. This is of particular concern for organic acids such as vanillic acid which are weakly retained on the HPLC column."

"This can be avoided/minimised by controlling the pH of the mobile phase. If this was not necessary it should be explained in the text."

The manuscript gave the misleading impression that we observed matrix effects. We did not. We have modified the text to improve clarity. Controlling the mobile phase pH had little effect on the analysis. We chose not to do this routinely because of the potential for increasing baseline noise due to the introduction of vanillic acid contamination from reagents.

Issue 8.

"Discussion of the results obtained on real samples is limited. Do you have the possibility to compare the results obtained with other proxies? I think that this would be a nice addition because the method itself is not innovative." We intentionally did not introduce comparisons with other paleofire proxies. This paper is intended to validate the methodology for measuring vanillic acid, not its use as a proxy. That is a far more complex task that will require considerable additional data from numerous sources. We are continuing to work on this issue, but are not prepared to make a statement about

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the relationship between vanillic acid and other proxies at this time.

Issue 9. Figure 4

“Figure 4 is not informative and can be removed. Values of slope, intercept and r2 of the linear regression (including uncertainties) would be more informative.”

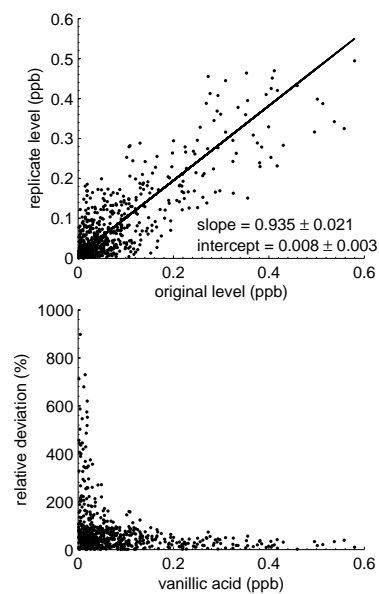
Figure 4 has been removed and the requested information has been added to the text.

The following reference will be added to the manuscript:

Zangrando, R., Barbaro, E., Zennaro, P., Rossi, S., Kehrwald, N.M., Gabrieli, J., Barbante, C., Gambaro, A., 2013. Molecular markers of biomass burning in arctic aerosols. *Environ. Sci. Technol.* 47, 8565–74. doi:10.1021/es400125r

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Student Version of MATLAB

Fig. 1. Figure 4

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