Atmos. Chem. Phys. Discuss., 15, C12102–C12105, 2016
www.atmos-chem-phys-discuss.net/15/C12102/2016/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "In situ measurements and modeling of reactive trace gases in a small biomass burning plume" *by* M. Müller et al.

M. Müller et al.

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Received and published: 29 January 2016

We thank reviewer #1 for her/his constructive comments on the manuscript.

COMMENT: On the detection of HONO as NO+, it seems to be there would be some issues relating to the reaction of NO+, native in the ion source as background, reacting with the high concentrations of VOC in the fire plume that would alter the background of NO+ in a non-quantifiable manner. To rephrase, NO+ will react reducing the background on that mass while in the plume, and performing a standard instrument zero cannot reproduce that reduction therefore increasing the error in your background subtraction. This would in effect, if my reasoning were correct, make the measurement of HONO a lower limit. Is there any way to potential approximate this effect, can the au-

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thors comment on the relative amount of NO+ in the ion source which is unavoidable? Or are then proportions such that one would not expect and NO+ + VOC reactions to occur. REPLY: The H3O+ and O2+ signals did not show any decrease when crossing the plumes. Given that O2+ is even more reactive than NO+, it is reasonable to assume that this also holds for the NO+ signal.

COMMENT: Also, the authors correct for HONO production on instrument surfaces, is this done using a laboratory measured conversion efficiency of 1%, or is this figure an approximation. This is important to state in the text when discussing the correction. REPLY: The revised manuscript includes further details: "A positive measurement artifact from NO2-to-HONO conversion (1 % of NO2) on instrumental surfaces was subtracted. The instrumental response to HONO and HONO inlet artifacts have been characterized in previous laboratory studies (Metzger et al., 2008; Wisthaler et al., 2003). Given that different inlet and drift tube configurations were used in those studies, the 1% NO2-to-HONO conversion efficiency is to be considered an upper limit estimate. Still, the NO2-artifact only accounts for 10.4% of the NO+ signal measured at the source."

COMMENT: The authors discuss the effect of large amounts of NO2 titrating O3 in the initial stages of the fire, but it seems the model does not pick this effect up (see figure 6). I assume this is why there is a steep drop in NO2 in the measurements prior to 600s. Why then is there not a corresponding increase in NO at this point, rather a drop in the measurements? Then the overall trend in the measurements for both NO2 and NO are increasing from 600s onward while the model shows a significant decrease in both mixing ratios. As the authors state in the text the model does a good job of capturing NO and NO2, this would seem to be a significant discrepancy, especially considering the log nature of the scaling. REPLY: It is NO that reacts with O3, not NO2.

COMMENT: Could the decrease in the methanol mixing ratio in the early stages of aging be a repartitioning of methanol to the aqueous phase of particles? There should be a fair amount of water vapor produced in the hot fire that would rapidly condense

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on existing particle phase. REPLY: The Henry's law constant of methanol is too small for this process to be important. We did not observe a decline in methanol even during convective injection events associated with heavy rainfall.

COMMENT: The comparison of the HONO emission ratio to previously available data is a very nice addition to the discussion of these results. I would urge the authors to consider explicitly adding additional comparisons to previously published emission ratios or factors to this manuscript. Another column on tables 2, 3 or S2 citing previous literature would be a very nice addition. Measurements of fuels from this region of Georgia have been performed before and would help to aid the connection of laboratory studies on biomass burning emissions with field observations such as these. I do not believe this is a necessary addition, but would be a welcomed addition to the work. REPLY: In the case of HONO, it was necessary to refer to the literature for obtaining increased confidence in our numbers. We had considered including literature values for VOCs until we realized that this would add a lot of complexity to the manuscript (large natural variability, impact of different fuels, impact of different burning conditions, comparability of results from laboratory and field studies, etc.). Given that this information is not strictly needed for conveying the scientific message of this study, we decided to keep the manuscript as concise as possible and did not include this discussion.

COMMENT: Page 31508, line 3: The use of the word tentative HONO here give the impression that the concentration used in this publication could change, or are preliminary. I suggest a different word choice. The Authors give good grounds for why the concentrations are reasonable, especially considering the agreement with previously published values. REPLY: "..., we generated tentative HONO data." has been replaced by ". . ., we made an attempt to quantify HONO emissions".

COMMENT: Page 31510, line 17: In reference to "compounds identified in previous studies" is a citation needed here? REPLY: "compounds identified in previous studies" has been replaced by "compounds identified in previous studies as detailed in paragraph 3.1.2".

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COMMENT: Page 31513, line 14: A comma is needed in 10,472 ppbC REPLY: Done.

COMMENT: Page 31514, line 15: There is a figure order issue here as figure 9a is mentioned prior to figure 6 it seems. REPLY: “see Fig. 9a” has been replaced by “see paragraph 3.2.2”

COMMENT: Page 31514, line 25: I believe you need to delete the word “respectively” REPLY: Done.

COMMENT: Figure 1: This is visually nice, but I am not entirely sure it is necessary in the manuscript. While seeing a fire plume is neat, it scientifically does not add to the discussion or conclusions. However, I am quite content leaving the decision up to the authors and the editor. REPLY: One important aspect of the paper is to demonstrate new measurement capabilities. The photos, together with Figure 3, illustrate that it is possible to resolve and study very small plumes. We also think that such a visualization may be useful for those who will be conducting similar studies in the future. Figure 2: Consider adding that the black arrows indicate the direction of flight to the caption. Done.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 31501, 2015.