Response to the comments of referee #2:

Comments on “Influence of biomass burning plumes on HONO chemistry in eastern China” by Nie et al.

This manuscript presents two-month measurements of HONO at a suburban site in the western Yangtze River delta, eastern China. The authors showed the influence of biomass burning plumes on the HONO concentrations and carefully discussed the potential mechanisms and implications. The interaction of atmospheric oxidants with aerosols is an important aspect of atmospheric sciences and the subject fits well the scope of ACP. Overall, I found this work interesting and promising. My only concern is that the increase of the HONO concentration or HONO/NOx ratio doesn’t necessarily mean an enhanced production. It can also be explained by reduced photolysis in the presence of thick plumes. I would recommend publication if the authors could address this problem and other issues as listed below.

General comments

The authors have discussed two kinds of effects of biomass burning plumes on the measured HONO concentrations: direct HONO emissions and secondary HONO formation from heterogeneous reactions. However, the aerosols plumes can attenuate the solar radiation leading to reduced photolysis and vertical mixing. This may also cause an accumulation of ground level HONO and elevated HONO/NOx. Due to fast photolysis, the daytime budget of HONO is quite different from that at the night time as reflected by their distinct HONO/NOx ratios (Qin et al., 2009; Sörgel et al., 2011). I am wondering if the day/night differences of HONO/NOx also exist in the present study. I would suggest the authors to include the solar radiation as another dimension in their analysis.

Response: First of all, we would like thank the referee for comments, especially for the constructive, helpful and specific suggestions on improving the manuscript.

We agree the photolysis of HONO would influence the ratio of HONO/NOx. To avoid this issue, we will only employ the nighttime dataset for the several comparisons in section 3.2 and 3.3 in the revised manuscript.

Specific comments

Page 7860 line 14: “A mixed plume of BB and anthropogenic fossil fuel (FF) emissions was observed on 10 June with even higher HONO concentrations and HONO/NO2 ratios.”

Response: We will change the employed dataset to the nighttime dataset for all the general BB episodes (except June 10th) in the revised manuscript in section 3.2 and 3.3 to avoid the possible influence of solar radiation. For the case of June 10th, the solar radiation was largely attenuated to a very low level (Ding, et al., 2013), we assume the photolysis of HONO can be ignored.

Page 7861 line 9: “Among these sources, heterogeneous processes are commonly accepted as the dominant, yet least understood, pathway to produce HONO.” If it is the
least understood pathway, it shouldn’t be accepted as the dominant source. I would suggest the authors to change this formulation.

Response: Agree. We will change the statement in the revised manuscript.

Page 7863 line 15: the stripping solution of WRD determines its sampling efficiency and potential artifacts. The authors should justify the use of H2O2 stripping solution. Genfa et al. (2003) could be a nice reference for this purpose, in which intercomparison was carried out to demonstrate the performance of H2O2 solution.

Response: Thanks for the suggestion.

We will add some description on the measurement issue and cite the recommended reference.

Page 7863 line 19: “The residence time of sampling air is actually very short in the sampling tubes (about 4.5 s) and WRD (about 0.2 s), the artifact caused by the NO2 conversion on the surface of the sampling tube and WRD solution is therefore small (Spindler et al., 2003).” If the short residence time is sufficient for complete absorption of HONO, it could be long enough for artifact production as well. However, I don't think artifacts should be a problem here. The use of acidic stripping solution has to a large extent avoided the formation of artifact NO2-. In addition, H2O2 can rapidly oxidize HSO3- and further inhibit the artifact reactions.

Response: Thanks for the suggestion.

We totally agree that H2O2 stripping solution would largely reduce the known interference by the NO2 and NO2+SO2. But, to minimize the possible positive interference, we will correct the dataset by the inter-comparison result of a WRD system and a LOPAP (Su, 2008).

Su, H: HONO: a Study to its Sources and Impacts from Field Measurements at the Sub-urban Areas of PRD Region, PhD thesis, Peking University, 2008.

Page 7863 line 26: it is better to mention that the NO2 measurements are subject to artifacts due to the use of the Molybdenum converter. This is important when comparing the present results (HONO/NO2) with other artifact-free measurement (e.g. DOAS).

Response: We totally agree, and will add this information in the revised manuscript.

Page 7864 line 19: can you also show the diurnal variation of HONO/NO2, HONO/NOx during BB and non-BB periods. Also I would suggest marking the BB and non-BB periods in Fig. 1.

Response: We will add the suggested diurnal variations in the revised manuscript.

As all the biomass burning events in the YRD region were induced by the agricultural fires which did not occurred continuously. For example, people preferred burning the straw in the night time due to the control of Chinese government. In addition, air masses were also needed to be in the “right” pathway from the BB source regions to the station when agricultural fires occurred. Therefore, the BB periods were not
continuous, but separated from each other, and thus difficult to be shaded in Figure 1.

Page 7864 line 21: “The samples with potassium concentrations higher than 2 μgm−3 and the ratio of potassium to PM2.5 larger than 0.02 were defined as BB samples, the remaining ones being categorized as non-BB samples.”. Can the authors explain why 2 μgm−3 and potassium to PM2.5 ratio of 0.02 were chosen as threshold values? Are these numbers critical for the conclusion? What the figure will look like if you plot hourly “HONO/NO2/particle surface areas” against “K+/PM2.5”?

Response: Based on our observation, the concentration of K+ is generally lower than 0.4 μg/m³ and K+/PM2.5 < 1% during the non-biomass burning periods. Here, considering the occasional agricultural fires (mostly occurred concentrated in the late May and early June) in the early summer around YRD, which provided a higher background value of K, we enhanced the criterions to K+ > 2 μg/m³ and K+/PM2.5 > 2% to ensure the observed plumes were influenced significantly by the BB.

We really thank the referee to raise the second comment, which is actually a very interesting issue. We think the purpose of the recommended plotting is to see the relationship of “HONO production efficiency” and “abundance of BB aerosols in the PM loadings”. If we select the nighttime dataset during BB, the value of “HONO/NO2/particle surface areas” generally decreased linearly along with the increase of “K+/PM2.5”. But we cannot conclude that “HONO production efficiency” decreased along with the increase of “abundance of BB aerosols in the PM loadings” (Fig. 1). It is, however, a more complex issue. Several parameters/relationships are involved in this relationship. First is the relationship between the “K+/PM2.5” and particle surface areas (Fig. 2). Second is the relationship between “HONO/NO2/particle surface areas” and particle surface areas (Fig. 3). Actually, when we look at the relationship of “HONO/NO2/particle surface areas” and “K+/PM2.5”, the involved parameters are assumed to be independent to each other, e.g. the particle surface and “K+/PM2.5”. However, as showed in the second figure below, particle surface areas are linear correlated to the “K+/PM2.5” (Fig. 2). Therefore, we do not think this plotting (Fig. 1) can nicely interpret the relationship of “HONO production efficiency” and “abundance of BB aerosols in the PM loadings”. Instead, we will add Fig. 3 in the revised manuscript to make this issue more clear.
Page 7865 line 16: “At least several hours were therefore needed before the BB emissions get to our measurement site, so the contribution of direct emissions to the observed HONO can be considered negligible.” Negligible means the life time of HONO is much shorter than the transportation time. Could you estimate the life time of HONO in the BB plumes? The radiation might be largely reduced in the presence of BB plumse and the life time might be longer than expected.

Response: We will add the lifetime calculation in the revised manuscript.

Page 7865 line 23: “no difference in the ground surface between the BB and non-BB periods during the campaign, the elevated HONO concentrations observed during BB episodes are expected to be due to aerosol-related heterogeneous processes.” and Page 7866 line 1: “Given that there was practically no difference ... to aerosol-related heterogeneous processes.”

As aforementioned, aerosol plumes could reduce the solar radiation and photolysis of HONO resulting in elevated HONO concentrations, which might also be able to explain the observations.

Response: We agree with the referee’s viewpoint and will change the dataset to the nighttime dataset in section 3.2 in the revised manuscript.

Page 7866 line 8: “In Fig. 7, we selected the samples ... The results showed a significantly larger surface area concentration for BB aerosols compared with non-BB aerosols.” In Fig. 7, is the difference in surface areas concentrations caused by the density difference or size distribution difference (between PM1 and PM2.5)?

Response: Yes. The difference in surface areas concentrations are caused by the
The differences of the size distribution and the particle numbers in the accumulation mode (especially in the range 100-300 nm).

Page 7866 line 19: “The values of this ratio were 40% higher during the BB period than that during non-BB period (Fig. 8), indicating a higher NO2 conversion efficiency of BB aerosols.”

The same concern as in my general comments.
Response: We will change the dataset used in this figure to the nighttime dataset.

Page 7867 Section 3.3: During the mix plume periods, the RH approached 90%. For the same PM2.5 (dry mass concentration), higher RH results in higher ambient PM concentration, thicker aerosol optical depth, and less radiation. Will it help to explain the higher HONO/NO2? I would also suggest including HONO/NO2 ratios into Fig. 11.
Response: Thanks for the referee’s suggestion. We will change the employed dataset of general BB episodes in Fig. 10 to nighttime data, and add some discussions on the issue.
The HONO/NO2 ratios will be added into Fig. 11 in the revised manuscript.

Page 7876 Figure 1: a comma is missing between NO2 and PM2.5.
Response: Will correct it in the revised manuscript.

**Technical corrections**
Page 7860 line 9: “was not associated ‘with’ potassium” Page 7860 line 11: “principle” or “principal”? Page 7861 line 22: do you mean “gaps”? Page 7860 line 18: “to HONO formation”, changed to “to the HONO formation” Page 7860 line 19: “suggests an important role of BB in atmospheric oxidation capacity”. Here “role in ... capacity” doesn’t sound good, you can say “suggests an important role of BB in atmospheric chemistry”
Response: We thank the referee for these technical comments, which will be corrected in the revised manuscript accordingly.

**Reference**