Response to the comments of referee 1:

General Comments

The authors present measurements of HONO, NO2, SO2, PM2.5 and some of its water-soluble components from a 2 month observational dataset in the Yangtze River delta. The HONO and water-soluble PM2.5 quantities presented have been made using the Monitor for Aerosols and Gases in Air (MARGA) platform. After separating the observations into biomass burning and non-biomass burning episodes, using particulate K+ as a tracer, the authors nicely show elevated mixing ratios of HONO in the biomass burning plumes that could impact the chemistry occurring therein and in entrained air masses that the plume encounters. The authors suggest, by data filtering and comparison, that observed enhancements in HONO/NO2 and HONO/NO2/submicron aerosol surface area in biomass burning plumes are demonstrative of enhanced NO2 to HONO conversion on these aerosol surfaces. There are only a few reports that have sufficient data to suggest direct observation of the aerosol heterogeneous conversion of NO2 process from field observations and this work adds significantly to this understanding. However, there are three major concerns that must be addressed before the conclusions of this manuscript are of sufficient quality to be considered for publication in Atmospheric Chemistry and Physics. First, the authors make an unfounded assumption that all HONO observed in their biomass burning plumes arises from secondary formation processes on aerosols and not direct emissions or from conversion on the ground surface, but they present data which contradicts this assertion. Second, there is insufficient evidence for the correction of known HONO interferences in wet chemical HONO methods from NO2 and SO2, nor is enough information given to be convincing that the MARGA platform has a quantitative collection efficiency of HONO. Third, data quantities in all comparisons are not given and frequently there are no plausible justifications for why the authors filtered their data for comparison in the way that they did.

Response: First of all, we would like thank the referee for the constructive, helpful and detailed comments and suggestions.

According to the comments, we modified the manuscript in the following aspects:

1) Provide more information in the measurement technology and data quality in the method part (Section 2.2 and 2.3);
2) Correct the data according to assumed interferences (New section 2.3) induced by the inlet and NO_2 based on one inter-comparison study conducted in China (see the response of the second major comment);
3) Change the dataset from whole dataset to the nighttime one in section 3.2 and 3.3 to avoid (1) the possible interference in the daytime samples and (2) the influence of HONO photolysis;
4) Add some statements to discuss the possible influence of direct emission (base on the HONO life time in the nighttime), and reactions on the ground surface in section 3.1. Model calculation using LPDM is employed to estimate the residence time of air masses at ground surface;
5) Add 2 sub-figures in Fig. 7 and Fig. 8 (New Fig. 8a and Fig. 10a) separately to interpret the reasons of the data selection for this two figures (see the response of the third major comment);
6) Add 3 new sub-figures (Fig. 11a-11c) to discuss on the possible influence of direct emission and atmospheric processing time on the enhanced HONO concentrations during the case of 10th June;
7) Add 3 sub-figures in Fig. 3 to compare the concentrations of $PM_{2.5}$, organic matters and NO_2 between BB and Non-BB.

In the following, we response the referee's comments item by item.

Specific Comments

Secondary HONO Formation Only on Aerosols

While HONO formation is most certainly occurring in the biomass burning plumes identified by the authors, the proportion of that HONO arising solely from heterogeneous conversion of NO2 on the surface area of the very high aerosol mass loadings of PM2.5 (> 100 _g m-3) is questionable. The authors make the assumption that all HONO observed in their biomass burning plumes arises from secondary formation processes on aerosols because HONO is so reactive that any directly emitted will be lost before arriving at the observation site, but they show in Figure 4 that fires where HONO will be emitted directly are easily within a 24-hour transport time to their observation site. Nocturnal and daytime transport of directly emitted HONO to the location of the measurements, depending on the advection distance, is therefore quite possible. This is particularly clear in the given June 10 case study where elevated mixing ratios of HONO on the order of 6 ppb were observed and the authors note that the HONO photolysisrate was probably suppressed due to the plume aerosol density. The authors' further statement that they consider the ground surface effect constant is also questionable because this will depend on the air mass trajectories when traveling from the biomass burning site to the field observation site and the time they spend in contact with the ground surface. It has been well established that NO2 reacts more effectively on real surfaces with increasing water coverage [Qin et al., 2009; Stutz et al., 2004], which will be different on a day-to-day basis as a function of temperature, relative humidity, irrigation, and precipitation. Furthermore, the objects located at the surface (e.g. soil, vegetation, buildings) encountered by the biomass burning plume will change the NO2 conversion efficiency for different air mass trajectories. Thus, longer contact times between the biomass burning plume would presumably lead to a greater ground effect on NO2 to HONO conversion. The authors should consider alternative explanations along with measurement data to account for their reasoning in stating that secondary conversion on aerosols is the only contributing factor to their HONO, HONO/NO2, HONO/NOx, and HONO/NO2/sub-micron aerosol surface area analyses or at least clearly present the data and/or calculations used to exclude the significance of alternative HONO sources contributing to their measurements. Emissions ratios of HONO from fossil fuel combustion (e.g. Table 1 in Kurtenbach et al. [2001]) and a variety of biomass sources (e.g. Figure 8 in Veres et al. [2010]) have been published, which may be useful in addressing this issue. The other works cited here for measurements at the Xianlin SORPES central site during this observation period [Ding et al., 2013a; Ding et al., 2013b] indicate that CO as a combustion tracer and solar irradiance for estimating photochemical loss of HONO in the biomass burning plumes are available to facilitate more detailed analyses of direct emissions and photolytic loss of HONO. Also, given that total PM2.5 mass and the water-soluble PM2.5 mass are being measured by the MARGA, are the authors able to estimate the organic fraction of the aerosol by mass difference? Are changes in the organic mass fraction of the PM2.5 in biomass burning plumes related to increases in HONO/NO2?

Response:

1）The issue of HONO direct emission from biomass burning:

I agree with the referee that biomass burning can emit some amount of HONO. In this work, the observation site was not around the source region of BB (Fig. 4). The calculated transport time was at least several hours. Below, we calculated the life time of HONO in the night time.

The loss of HONO at night mainly include the below path ways: a) the depression of HONO on ground; b) the heterogeneous loss of HONO on aerosol; c) the $HONO+OH \rightarrow H_2O+NO_2$ (Li et al., 2012). For loss path a), $\tau_a = \frac{1}{k_a} = \frac{H}{V_{HONO}}$. The dry deposition of HONO 0.8 cm s^{-1} was taken with the mixing height of 100m (Li et al., 2012). For loss path b), $\tau_b = \frac{1}{k_b} = \frac{1}{\frac{1}{4} * \gamma_{HONO} s_{aerosol} * \overline{v_{HONO}}}$. The HONO uptake coefficient on aerosol was estimated as 10^{-3} (Wong et al., 2011), the aerosol surface during observation was about $1.5*10^{3}$ $\mu m^2/cm^3$, the mean molecular velocity of HONO was about 380m/s. For loss path c), $\tau_c = \frac{1}{k_c} = \frac{1}{k*OH}$. The OH concentration was estimated as 10^6 mol cm^{-3}(Hofzumahaus et al., 2009) and $K_{HONO+OH}$ of $5.0*10^{-12}$ cm^3 s^{-1} at 298k (Sander et al., 2006) was adopted. In these conditions, $\frac{1}{\tau} = \frac{1}{\tau_a} + \frac{1}{\tau_b} + \frac{1}{\tau_c}$ the lifetime of HONO was estimated about 1.5 hours.

According to the LPDM simulations, the transport time from the fire regions to the observation site are generally larger than 6 hours. Therefore, considering a lifetime of about 1.5 hours, we believe the contributions of direction emission to the observed enhanced HONO concentrations were not significant.

2）Base on the calculated HONO lifetime, we calculated contact time and residence regions of air plumes with the ground surface.

In the revised manuscript, we added some statement in section 3.2.1 to discuss the influence of direct emission and ground surface.

Reference:

Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner, A., and Zhang, Y.: Amplified Trace Gas Removal in the Troposphere, Science, 324, 1702-1704, 2009.

Li, X., Brauers, T., Häseler, R., Bohn, B., Fuchs, H., Hofzumahaus, A., Holland, F., Lou, S., Lu, K. D., Rohrer, F., Hu, M., Zeng, L. M., Zhang, Y. H., Garland, R. M., Su, H., Nowak, A., Wiedensohler, A., Takegawa, N., Shao, M., and Wahner, A.: Exploring the atmospheric chemistry of nitrous acid (HONO) at a rural site in Southern China, Atmos. Chem. Phys., 12, 1497-1513, 2012.

Sander, S. P., Golden, D., Kurylo, M., Moortgat, G., Wine, P., Ravishankara, A., Kolb, C., Molina, M., Finlayson-Pitts, B., and Huie, R.: Chemical kinetics and photochemical data for use in atmospheric studies evaluation number 15, 2006. 2006.

Wong, K. W., Oh, H. J., Lefer, B. L., Rappenglück, B., and Stutz, J.: Vertical profiles of nitrous acid in the nocturnal urban atmosphere of Houston, TX, Atmos. Chem. Phys., 11, 3595-3609, 2011.

Sampling Interferences, Collection Efficiency and Suitable Corrections

The detail provided in Section 2.2 on Measurement techniques is not sufficient to demonstrate that this HONO measurement is reliable. How was the MARGA calibrated for quantifying HONO? Were aqueous nitrite standards injected on the ion chromatograph or was a gas-phase HONO source [Febo et al., 1995] used to account for collection, transport, and stability to the IC from the wet rotating denuder (WRD)? Has the magnitude of chemical transformation of nitrite (NO2-) to nitrate (NO3-) by reaction with the 10 ppm H2O2 in the WRD been quantified? What is the HONO collection efficiency of 10 ppm H2O2 solution in the WRD? To my knowledge, the MARGA platform has not been validated by offline assessment of its HONO collection efficiency or in-field comparison with an established instrument and raises concerns towards the accuracy of the HONO measurement. Do the authors have any data to present to this effect?

Response: We have provided some information in the revised manuscript on the measurement issues.

As we did not have a HONO source, we only calibrated the MARGA HONO with aqueous nitrite standards. For the issue of chemical transformation of nitrite to nitrate, both Applikon Company and ourselves did do some lab experiments to assess it. The first test is injecting NO_2 with peroxide to see if nitrate was developed. The results did not show any production of nitrate even with a wide range of NO_2 concentration from10 ppb to 10 ppm. The second test was to inter-compare the HONO measurements with water and peroxide as the solution liquids, respectively. The results showed no difference.

We agree with the referee that there are not any publications to assess the HONO collection efficiency of the MARGA platform. But as one of the wet denuder, many studies have suggested its collection efficiency was higher than 95% (Part 3 in the book of Ian Barnes and Krzysztof J. Rudziński, 2012, and the references therein). During our measurements (more than 1 year, up to now), we hardly observed the nitrite in the aerosol phase even at the period of high HONO concentrations, suggesting a high collection efficiency of MARGA to the gas phase HONO with the absorption solution. In addition, there has been a publication (Makkonen et al., 2014) which reported one year’s measurement of HONO using MARGA, and showed reasonable values and characters.

Reference:

Ian Barnes, K. J. R., Disposal of Dangerous Chemicals in Urban Areas and Mega Cities Role of Oxides and Acids of Nitrogen in Atmospheric Chemistry. Springer, 2013.

Ulla Makkonen, A. V., Heidi Hellén, Marja Hemmilä, Jenni Sund,, Mikko Äijälä, M. E., Heikki Junninen, Petri Keronen,, Tuukka Petäjä, D. R. W., Markku Kulmala and, and Hakola, H.: Semi-continuous gas and inorganic aerosol measurements at a boreal forest site: seasonal and diurnal cycles of NH3, HONO and HNO3, Boreal

Environment Research, 1797-2469 (online), 2014.

Were the MARGA background signals in NO2- assessed during the observation period reported here? If so, how were the backgrounds collected and what was the magnitude of any corrections made to the reported HONO dataset?

Response: We have injected the ultrapure water into MARGA for several times. There was not any NO_2^- signal at all.

Finally, the authors state that production of interfering HONO signal from NO2 conversion on the WRD is small, citing Spindler et al. [2003] who used a 1mM, pH 10, K2CO3 stripping solution in a wet annular denuder. Has a correction has been made to the presented dataset based on the cited study? Has the NO2 interference for this MARGA been measured independently to support this approach since the denuder solution compositions are different? Has other published work on the NO2 interference been considered (e.g. Mertes and Wahner [1995])? Assuming applicability of the interference findings from Spindler et al. [2003] to the MARGA platform, an estimate of the HONO interference can be made by using a representative estimate of the NO2 (20 ppb) and SO2 (5 ppb) mixing ratio data presented in this work - and also reported in the other SORPES datasets [Ding et al., 2013a; Ding et al., 2013b] - to demonstrate that corrections are required: a calculated interference of 0.44 ppb HONO that could be expected for much of this dataset if an uncorrected interference is present.

Response: Generally, the interference of the WRD technique was from the NO_2 reaction on the wet surface (wall of the sampling tube and the surface of the solution in WRD), which can be enhanced if there is S (IV) in the absorption solution.

In this study, 10 ppm H_2O_2 was employed as the absorption solution in the MARGA system, which can largely reduce the interference. Firstly, H_2O_2 can rapidly oxidize HSO_3^- and inhibit the artifact reactions of NO_2 and S (IV) in the aqueous phase. This result had been demonstrated by Genfa et al. (2003). Secondly, the formed H_2SO_4 via the oxidation of HSO_3^- would make the absorption solution being acidic, which will suppress the NO_2 reaction on the surface to some extent.

There were several assessments or comparisons of the WRD technique with other techniques, e.g. LOPAP and DOAS. All these comparisons showed good correlations, and some overestimation for the WRD technique only in the daytime (Appel et al., 1990; Müller et al., 1999; Spindler et al., 2003).

Therefore, in the revised manuscript, we added more statement on the technique issue, corrected the dataset by the inter-comparison result (Su, 2008) and changed the employed dataset from the whole dataset to the nighttime dataset in section 3.2 and 3.3.

Reference:

Appel, B. R.; Winer, A. M.; Tokiwa, Y.; Biermann, H. W., Comparison of atmospheric nitrous acid measurements by annular denuder and differential optical absorption systems. *Atmospheric Environment. Part A. General Topics* **1990,** *24* (3), 611-616.

Th. Muller, R. D., G Spindler, E Bruggemann, R. Ackermann, A. Geyer, U. Platf, Measurements of Nitrous Acid by DOAS and Diffusion Denuders: A Comparison. *Transactions on Ecology and the Environment* **1999,** *28*, ISSN 1743-3541.

Genfa, Z., Slanina, S., Brad Boring, C., Jongejan, P. A. C., and Dasgupta, P. K.: Continuous wet denuder measurements of atmospheric nitric and nitrous acids during the 1999 Atlanta Supersite, Atmospheric Environment, 37, 1351-1364, http://dx.doi.org/10.1016/S1352-2310(02)01011-7, 2003.

Spindler, G., Hesper, J., Brüggemann, E., Dubois, R., Müller, T., and Herrmann, H.: Wet annular denuder measurements of nitrous acid: laboratory study of the artefact reaction of NO2 with S(IV) in aqueous solution and comparison with field measurements, Atmospheric Environment, 37, 2643-2662, http://dx.doi.org/10.1016/S1352-2310(03)00209-7, 2003.

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.

Data Quantities in Comparisons of Filtered Data

Throughout the manuscript, the total number of data points used in the analyses are not given. This is cause for concern because Figures 3, 7, 8 and 10 all utilize subsections of the presented dataset. Additionally, the reasoning for some filtering of the datasets is unjustified and comes across as arbitrary instead of by informed decision making. For instance, what fraction of the data is classified as biomass burning by applying the > 2 _g m-3 K+ filter and why was this criterion used? K+ is a well-established biomass burning tracer, but the reasoning for the mass loading filter is not provided with the expected referencing to literature precedents. The caption in Figure 4 suggests that a ratio of K+/PM2.5 > 2 % was also used, but is not presented in the text.

Response: We have provided the information of total sample number in the revised manuscript.

For the issue of defining the biomass burning event, the criterions were $K^+ > 2$ μg/m^3 and $K^+/PM_{2.5} > 2\%$. Only the samples which satisfy the two criterions, we defined them as biomass burning samples. The samples with both $K^+ < 2$ μg/m^3 and $K^+/PM_{2.5} < 2\%$ were categorized as non-biomass burning samples. We described this point in the second paragraph in section 3.1.

We agreed to the referee's comment that there is not a unique criterion to define the biomass burning plumes. Generally, based on our observation, the concentration of K^+ is lower than 0.4 μg/m^3 and $K^+/PM_{2.5} < 1\%$ 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/m^3 and $K^+/PM_{2.5} > 2\%$.

Similarly, when subsequent filters (e.g. PM2.5 mass of 100 – 150 _g m-3 for Figure 7a and 1.5 – 2.2 x 10-9 m2 cm-3 for Figure 8) are applied to both biomass burning and non-biomass burning, the reasoning for doing so is not given or poorly justified (e.g. because BB and NBB have overlapping surface areas in the 1.5-2.2 x 10-9 m2 cm-3 range). There must be some plausible rationale for why some of the figures presented include the data shown and exclude the rest of the data from the comparison. For example, why aren't all of the BB and NBB data points used for the plot in Figure 7b? What aerosol or BB properties are being explicitly selected for by isolating the PM2.5 mass loadings in the 100 – 150 _g m-3 range? How many data points remain in the comparisons? If it is a small number of points in the Figure 7 and 8 comparisons, then does this mean clear HONO production on aerosol surfaces was an infrequent observation?

Response: For Figure 7, our aim was to compare the specific surface area (the concentration ratios of surface area to mass) of biomass burning and non-biomass burning plumes. As it is not linear relationship between particle surface areas and masses (see following Fig. 1, Fig. 8a in the revised manuscript), it is more reasonable to select a similar mass concentration range to compare their surface areas. For example, in the study, mass concentrations of non-biomass burning samples were generally lower than 150 μg/m^3 (mostly lower than 100 μg/m^3 with the mean value of 60 μg/m^3), however, the mass concentrations of biomass burning samples were higher than 100 μg/m^3 (mostly higher than 150 μg/m^3 with the mean value of 174 μg/m^3, see following Fig. 1). If we selected the whole dataset to compare their surface areas, the BB samples would definitely show much higher values than those of Non-BB samples (figure not shown), but it did not suggest a higher specific surface area. Therefore, we selected the overlap parts of mass concentrations between BB and Non-BB periods, and the distributions of selected mass concentrations did not show statistically significant difference. It also can be clearly showed in the following Fig. 1, the specific surface areas (particle surface areas/PM$_{2.5}$) of Non-BB aerosols are anti-correlated to the particle concentrations. However, the data points for BB samples are not in this fitting curve, but show significant enhanced values.

In the revised manuscript, we added the following figure and some statements to interpret this issue more clearly.

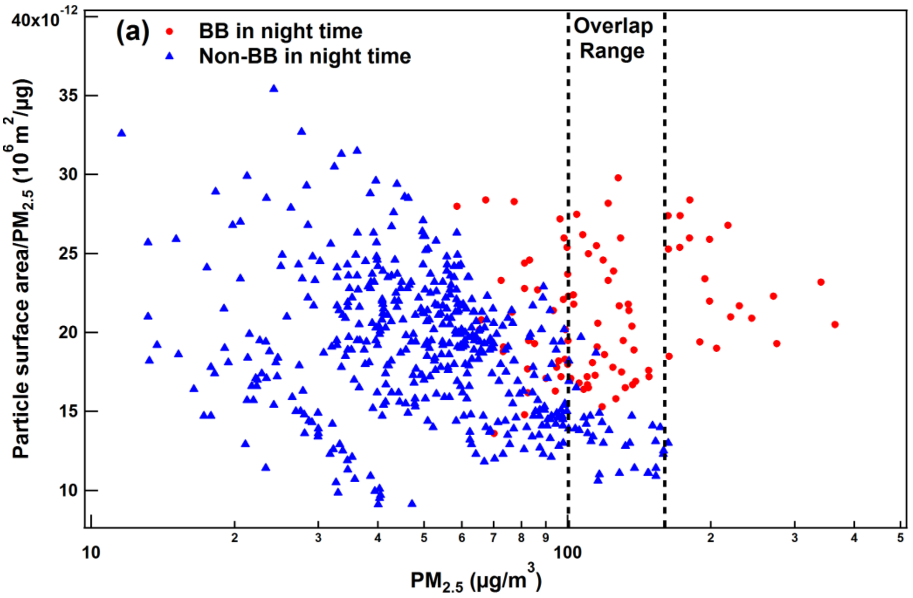

Fig. 1

In the revised manuscript, we changed the dataset to night time dataset, the number of data points deployed in this Figure 7 (new Fig. 8) was 51 for BB samples, and 27 for NBB samples. We have added this information in the figure capture of Figure 7 (New Fig. 8).

The data selection for Figure 8 (New Fig. 10) was in the same case of Figure 7 (new Fig. 8). We did not know whether the relationship of HONO/NO_2 and particle surface area is liner or not (possibly not). As showed in the following Fig. 2, "HONO/NO_2/particle surface areas" is anti-correlated to the particle surface areas in a power fit. So we believed it was more reasonable to select a similar concentration range of surface area to make this kind of comparison. We have added the following Fig. 2 in the revised manuscript (New Fig. 10a) to interpret this issue more clearly.

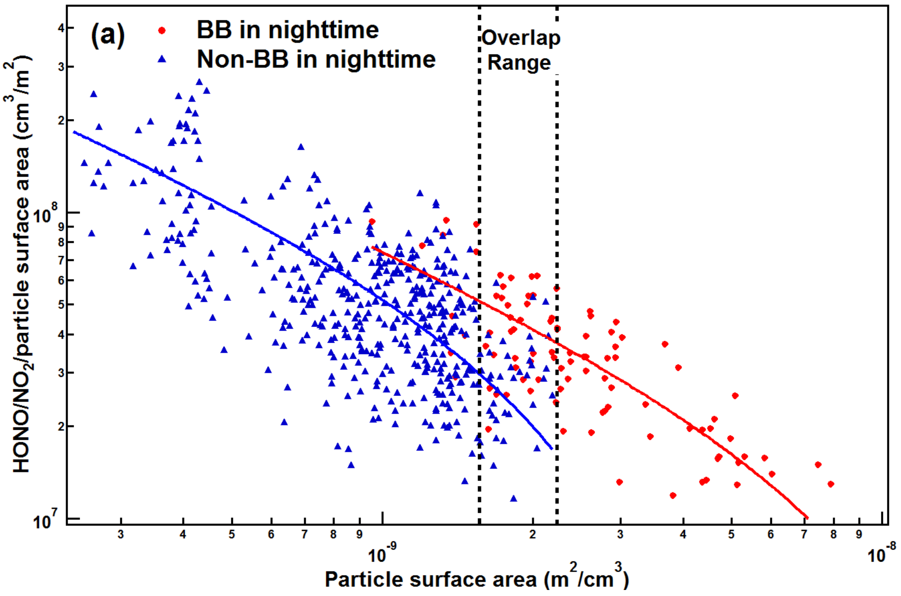

Fig. 2

In the revised manuscript, after we changed the dataset to night time data, the number of data points deployed in this Figure 8 (New Fig. 10) was 35 for BB samples, and 51 for NBB samples. We have added this information in the figure capture.

Other Concerns

Page 7861, Lines 14-18: Only NO2 on wet surfaces applies to nocturnal production. The rest tend to require photoexcited substrates. Also, TiO2 in mineral dust has also been shown as a potential HONO source by heterogeneous reaction of NO2 (e.g. [Bedjanian and El Zein, 2012; Langridge et al., 2009]).

Response: Have added the suggested references to the revised manuscript.

Page 7861, Lines 27-29: The experiments of Aubin and Abbatt [2007] used synthetic hydrocarbon fuels, not biomass. More appropriate references for biomass burning HONO emissions are: [Roberts et al., 2010; Veres et al., 2010].

Response: Have changed the references in the revised manuscript.

Page 7862, Lines 1-4: The fate of HONO in an aging biomass burning plume stated here may be true for transport during the day, but the dominant loss to photolysis is not present at night. What is the relevant reference for these statements?

Response: We refer to our response of major comment 1. We have calculated the nighttime lifetime of HONO and added the information in the revised manuscript (Section 2.4).

Page 7862, Lines 1-14: It seems unnecessary to devote an entire paragraph to the impacts of soot in the introduction when a soot measurement is not presented in the data analysis of this manuscript.

Response: We have simplified the statements in the revised manuscript.

Page 7864, Lines 23-26: These three parameters cannot be said to have been positively impacted by biomass burning aerosols unless the dataset can be decoupled from other HONO sources. Otherwise, it can be contested that these measurements are just higher HONO observations in biomass burning plumes from direct and secondary HONO sources compared to the regional background HONO levels.

Response: In this paragraph, we did not conclude that the "biomass burning aerosols" but the "biomass burning plumes" positively impact the HONO. We have added the word "plumes" in the revised manuscript.

Page 7865, Lines 10-12: Veres et al. [2010] have provided a comprehensive summary of HONO/CO emissions ratios for biomass burning experiments, ranging from 0.95 – 4 mmol mol CO-1. Can the presence of direct emissions of HONO be excluded from nocturnal observations using this information?

Response: Thanks for the suggestion. As calculated in the former response, even in the night time, the life time of HONO is only about 1.5 hours in YRD regions. Therefore, we believe the contributions of HONO from direct emissions of BB to the aged plumes can be ignored.

We have added some statement for this issue in the revised manuscript.

Page 7865, Lines 12-14: Figure 2 shows a persistent 0.5 ppb of HONO during the daytime, so how is the statement made in this sentence justified?

Response: We have changed the statements in the revised manuscript, and added the information of HONO lifetime calculation.

Page 7865, Lines 20-23: What happens to the correlation shown in Figure 5 if only the nocturnal data points are considered? Can a similar conclusion reached using CO? Wouldn't daytime HONO loss to photolysis confound the correlative investigation here since K+ does not have a similar photolytic sink? Is there a better biomass burning tracer that could be used during the day?

Response: We have changed the deployed dataset to the nocturnal data in Figure 5, which showed similar results.

In the revised manuscript, we have changed the whole dataset to nighttime dataset in section 3.2 and 3.3.

Page 7865, Line 25: Figure 1 does not show this data clearly. A separate plot should be made to demonstrate this and it could be added as a fourth panel to Figure 3.

Response: We have added a new sub-figure of Fig 3c to compare the nocturnal NO_2 concentrations between the BB and NBB periods.

Page 7866, Lines 1-4: There is no direct evidence presented to justify this statement. See major comments above on additional considerations necessary to make these assumptions.

Response: We refer to our response of the major comment 1.

Page 7866, Line 5: At no point in this manuscript is the fraction of the total data that is classified BB vs NBB given. Besides stating this explicitly, shading the BB periods in Figure 1 can also aid in conveying the relative incidence of BB plumes at the sampling site.

Response: The criterion to classify BB and non-BB was given in the 2nd paragraph of section 3.1.

"The samples with potassium concentrations higher than 2 μg m^{-3} and the ratio of potassium to $PM_{2.5}$ larger than 0.02 were defined as BB samples. The samples with potassium concentrations lower than 2 μg m^{-3} and the ratio of potassium to $PM_{2.5}$ smaller than 0.02 were categorized as non-BB samples."

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 duo 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 7866, Lines 8-14: This is the best evidence given in this manuscript for separating BB and NBB using the K+ observations or making the assertion that aerosols are influencing HONO chemistry in BB plumes. This should follow on the justification statements to be added for the K+ filtering to clearly demonstrate that these air masses have significantly different aerosol populations. However, as pointed out above, this point becomes moot if the mass range screening of the data from 100-150 _g m-3 is arbitrary. Why was this mass range selected instead of comparing the entirety of the two aerosol population measurements?

Response: We refer to our response to the major comment 3. Again, if we choose the whole dataset, the surface area concentrations of BB aerosols will show much higher values than those of NBB aerosols. And the differences will be much larger than those showed in Fig. 7b (New Fig. 8c) due to both the larger specific surface area and much higher particle mass loadings.

Page 7866, Lines 15-16: This sentence is followed by a discussion on the surface area, not the chemical nature.

Response: Agree. We have changed this sentence to the end of last paragraph in the revised manuscript.

Page 7866, Line 27 – Page 7867, Line 2: Soot mass loading was not measured, or at least presented, from this field site, so this statement is conjecture.

Response: We agree that we did not have direct evidence to support this statement. But, there were many studies had demonstrated that soot particles are one of the major components of BB aerosols. And our following studies in 2013 and 2014 did show significantly enhanced concentrations of blank carbon and organic carbon.

Page 7867, Lines 2 – 5: These statements follow on comparisons derived from an arbitrary surface area range selection from within an arbitrary mass loading filter applied to this dataset. Why not try to reconcile with PM2.5 organic fraction by mass difference in the PM2.5 mass and MARGA water-soluble mass measured?

Response: Agree. We have added this information and a sub-figure (Fig. 2b) in the revised manuscript.

"This is supported by the much higher concentrations of organics and black carbons, which were estimated as the differences of $PM_{2.5}$ *and the water soluble ions, in BB periods than those in Non-BB periods (see Fig. 3b)."*

Page 7867, Lines 9-13: This observation calls into question the previous assumption of HONO reactivity and loss in BB plumes throughout the manuscript.

Response: We refer to the calculation of HONO nighttime lifetime in our response to major comment 1.

Page 7867, Lines 14-16: The June 10 event looks to be about 3 times longer in duration than any other elevated PM2.5 events reported. What is the influence of a longer NO2 contact time with the available particulate surface area? How much HONO production could this account for?

Response: We agree that the NO_2 contact time with the particulate surface would influence the HONO production. But this contact time should not be the duration of the episodes we observed, but the transport time of the plumes. In the revised manuscript, we calculated the ratios of nitrate to NO_y to estimate the atmospheric processing time. The results showed similar values for both the June 10th event and other general BB episodes.

We have added some sentences and 2 sub-figures (new Fig. 11b and 11c) to describe this point.

Page 7867, Lines 20-25: How can the effect of transport time be accounted for in this analysis? Have the authors plotted HONO vs K+ or CO for this event to look for evidence of direct emissions consistent with the literature? How aged was the plume at the different observation times? Could the changing slopes reflect longer reaction times of NO2 on the aerosols before reaching the site?

Response: We agree with the referee's viewpoint. And have added 3 new sub-figures (new Fig. 11a-11c) and a few sentences to state the influences of direct emission and transport time on the HONO concentrations during the event of 10th June.

"Again, we investigated the relation between HONO and potassium. The result showed poorly correlation (Fig. 11a), suggesting that the enhanced HONO concentrations during the case of 10 June were secondarily produced. Although a high particle loading should be a contributor to the high HONO levels, it was not likely the most predominant factor because the PM concentrations during this event were comparable to the peak concentrations during the other BB episodes (Fig. 1). Another possible reason is that the plumes on 10 June were more aged than the other BB plumes, which would enhance the HONO production with a longer NO_2 *contact time with aerosol surface. Here, we deployed the ratio of nitrate to* NO_y *to estimate the atmospheric processing time. As shown in Fig. 11b and 11c, all the BB plumes were in the same regime (Fig. 10b), and the values were similar, suggesting that there were no significant differences of atmospheric processing time for both general BB*

plumes and 10 June case."

Page 7867, Line 27 – Page 7868, Lines 1-7: These conclusions are not sound. The plume transport time is not known, a conservative tracer of direct HONO emissions is not employed, and the aerosol surface area and composition is not measured or reported, respectively.

Response: We refer to our response to the former comment.

Page 7868, Lines 8-15: As discussed above, SO2 is a known contributor to the NO2 interference for HONO measurements when using wet chemical gas sampling techniques, such as the wet rotating denuder [Spindler et al., 2003]. Given that this event witnessed > 10 ppb of SO_2, there needs to be greater certainty that the appropriate corrections to the HONO measurement have been made.

Response: The interference by SO_2+NO_2 for HONO measurement is induced by the reaction of S (IV) (in the liquid phase) and NO_2. For the MARGA system, 10 ppm H_2O_2 was used as the absorption solution, which can oxidize the S (IV) very quickly. Therefore, the additional interference caused by the SO_2+NO_2, which was observed with other absorption solution (e.g. K_2CO_3), can be avoided in the MARGA system. This result has been demonstrated in the lab study (Genfa et al., 2003). We have add some statement on the issue in the method part (Section 2.3).

Reference:

Genfa, Z., Slanina, S., Brad Boring, C., Jongejan, P. A. C., and Dasgupta, P. K.: Continuous wet denuder measurements of atmospheric nitric and nitrous acids during the 1999 Atlanta Supersite, Atmospheric Environment, 37, 1351-1364, http://dx.doi.org/10.1016/S1352-2310(02)01011-7, 2003.

Page 7869, Lines 4-6: This should have a literature reference. However, there is good basis in the literature to state the opposite. Kleffmann et al. [1998] showed that SO42-- containing substrates, representative of atmospheric aerosols, can convert NO2 to HONO at a similar rate to that observed by Kurtenbach et al. [2001] and used in 1D

HONO models, such as that of Wong et al. [2011].

Response: We agree with the referee’s viewpoint, and have changed the statement in the revised manuscript.

“Another factor that might enhance HONO production might be the formation of some specific secondary material on BB particles, e.g. sulfate (Kleffmann et al., 1998) and secondary organic aerosols (Bröske et al., 2003).”

Figure 6: Why have the authors not plotted HONO/NO2 vs surface area here?

Response: One major purpose of this figure was to show the correlation of NO_2 and HONO, which cannot be interpreted by the plot of HONO/NO_2 vs surface area.

Figure 7: n = ?. Looking at Figure 1 suggests that there are very few data points being used in this comparison. Why the 100-150 _g m-3 filter applied to the dataset and not comparing the entire BB vs NBB like in the rest of the manuscript?

Response: We have added the samples number in the figure capture in the revised manuscript, and added a new sub-figure to interpret this issue (new Fig. 8a). For the reason we chose the 100-150 μg/m^3 filter, we refer to our former response to the major comment 3.

Figure 8: n = ?. If this is a subset of the data in Figure 8 by selecting for 1.5-2.2 x 10-9 m2 cm-3 surface area, that means there is possibly even fewer data points being compared here than in the previous figure. Why not compare the entire BB and NBB datasets here as well?

Response: We have added the samples number in the figure capture in the revised manuscript, and added a new sub-figure to interpret this issue (new Fig. 10a). For the reason we chose overlap concentration range of surface area, we refer to our former response to the major comment 3.

Figure 9: The exact times of the June 10 case considered should be given. It appears

that they span from June 9 through June 11. Furthermore, the criteria for the event to be ‘beginning’ or ‘later’ should be clearly stated. By looking at the data in Figure 11, the slope presented for the ‘later’ stage data points seems to be driven mostly by the three lowest data values, which do not coincide with any other parameter presented in Figure 11. It would seem that the event is being defined by the intrusion of high PM2.5 mass loadings > 150 _g m-3. If so, why are these three points not considered ‘beginning’ points? What is the slope if they are removed from the ‘later stage’ analysis?

Response: We have given the exact times of June 10 case in the revised manuscript. The beginning stage was defined as the first 5 hours when the BB plume of this case arrived out station. We have added this information in the revised manuscript.

The three lowest data point did influence the slope of the later stage. If we remove them, the slope will change from 0.15 to 0.12, which are still much higher than the other BB episodes.

Figure 10: Again, no reasonable justification for selecting the narrow mass loading range.

Response: We refer to our response of the major comment 3. For this figure, the PM mass concentrations were generally higher in the case of June 10th than those in other BB episodes. Therefore, we selected the overlap range to avoid the interference induced by the difference of mass concentrations.

Figure 11: There are 17 data points on this plot. This means that there is more than one night being plotted here. What period of time are these points from?

Response: We have given the exact times of June 10 case in the revised manuscript.

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 westernYangtze River delta, eastern China.The authors showed the influence of biomass burningplumes 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/NO_x. To avoid this issue, we employed 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.*" Is it because higher PM concentrations reduced solar radiation and the photolytic sinks

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

Reference:

Ding, A. J., Fu, C. B., Yang, X. Q., Sun, J. N., Petäjä, T., Kerminen, V. M., Wang, T., Xie, Y., Herrmann, E., Zheng, L. F., Nie, W., Liu, Q., Wei, X. L., and Kulmala, M.: Intense atmospheric pollution modifies weather: a case of mixed biomass burning with fossil fuel combustion pollution in eastern China, Atmos. Chem. Phys., 13, 10545-10554, 10.5194/acp-13-10545-2013, 2013.

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 have changed 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 have added some description on the measurement issue and cited the recommended reference in section 2.

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 H_2O_2 stripping solution would largely reduce the known interference by the NO_2 and NO_2+SO_2. But, to minimize the possible positive interference, we corrected the dataset based on the inter-comparison result of a WRD system and a LOPAP (Su, 2008).

Reference:

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 have added this information in the revised manuscript (Section 2.2).

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 have added the diurnal variations of HONO/NO_2 in the revised manuscript. As BB episodes were mostly observed in nighttime (except the case of 10 June), we did not give the diurnal variations separately during BB and Non-NN periods.

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 duo 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 marked 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/m^3 and $K^+/PM_{2.5}$ < 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/m^3 and $K^+/PM_{2.5}$ > 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/NO$_2$/particle surface areas” generally decreased linearly along with the increase of “K+/PM$_{2.5}$”. 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$^+$/PM$_{2.5}$” and particle surface areas (Fig. 2). Second is the relationship between “HONO/NO$_2$/particle surface areas” and particle surface areas (Fig. 3). Actually, when we look at the relationship of “HONO/NO$_2$/particle surface areas” and “K$^+$/PM$_{2.5}$”, the involved parameters are assumed to be independent to each other, e.g. the particle surface and “K$^+$/PM$_{2.5}$”. However, as showed in the second figure below, particle surface areas are linear correlated to the “K$^+$/PM$_{2.5}$” (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.

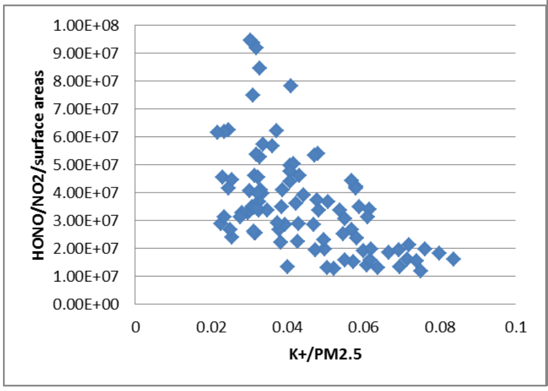

Fig. 1

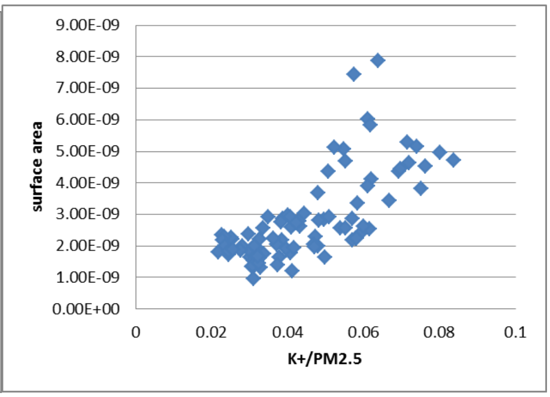

Fig. 2

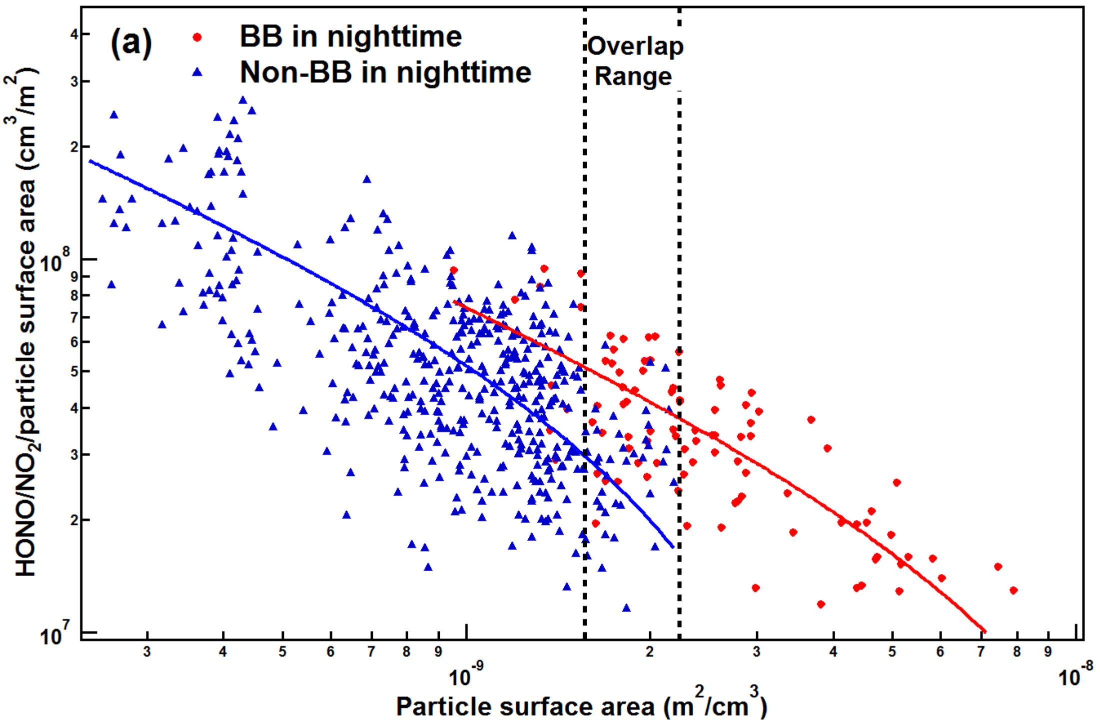

Fig. 3

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 have added the lifetime calculation in Section 2.4 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 have changed 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 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 have changed 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 have changed the employed dataset of general BB episodes in Fig. 10 (New Fig. 13) to nighttime data, and add some discussions on the issue in the revised manuscript.

The HONO/NO_2 ratios have been added into Fig. 14 in the revised manuscript.

Page 7876 Figure 1: a comma is missing between NO2 and PM2.5.

Response: Have corrected 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 have been corrected in the revised manuscript accordingly.

Reference

Genfa, Z., Slanina, S., Brad Boring, C., Jongejan, P. A. C., and Dasgupta, P. K.: Continuous wet denuder measurements of atmospheric nitric and nitrous acids during the 1999 Atlanta Supersite, ATMOSPHERIC ENVIRONMENT, 37, 1351-1364, http://dx.doi.org/10.1016/S1352-2310(02)01011-7, 2003.

Qin, M., Xie, P. H., Su, H., Gu, J. W., Peng, F. M., Li, S. W., Zeng, L. M., Liu, J. G., Liu, W. Q., and Zhang, Y. H.: An observational study of the HONO-NO2 coupling at an urban site in Guangzhou City, South China, Atmospheric Environment, 43, 5731-5742, 10.1016/j.atmosenv.2009.08.017, 2009.

Sörgel, M., Trebs, I., Serafimovich, A., Moravek, A., Held, A., and Zetzsch, C.: Simultaneous HONO measurements in and above a forest canopy: influence of turbulent exchange on mixing ratio differences, Atmos. Chem. Phys., 11, 841-855, 10.5194/acp-11-841-2011, 2011.