Response to the comments of referee # 1:

General Comments

The authors present measurements of HONO, NO_2, SO_2, $PM_{2.5}$ and some of its water-soluble components from a 2 month observational dataset in the Yangtze River delta. The HONO and water-soluble $PM_{2.5}$ 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/NO_2 and HONO/NO_2/submicron aerosol surface area in biomass burning plumes are demonstrative of enhanced NO_2 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 NO_2 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 NO_2 and SO_2, 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 will modify the manuscript in the following aspects:

1) Provide more information in the measurement technology and data quality in the method part;
2) Correct the data using assumed interferences 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 one paragraph 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 will be employed to estimate the residence time of air masses at ground surface and from different land cover categories;

5) Add 2 sub-figures in Fig. 7 and Fig. 8 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. 10a-10c) 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→H_2O+NO_2 (Li et al., 2012). For loss path a), $\tau_a = \frac{1}{k_a} = \frac{1}{\frac{H}{v_{HONO}}}$. 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^{-4} (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 accounts 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 will calculate contact time of air plumes with the ground surface and the estimate the difference of the land cover for different transport pathways.

In the revised manuscript, we will add a paragraph 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 (NO_2^-) to nitrate (NO_3^-) by reaction with the 10 ppm H_2O_2 in the WRD been quantified? What is the HONO collection efficiency of 10 ppm H_2O_2 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 will provide 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 solution liquid. 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 NO2- 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 NO2 reaction on the wet surface, 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 will add more statement on the technique issue, correct the dataset by the inter-comparison result (Su, 2008) and change the employed dataset from the whole dataset to the nighttime dataset in section 3.2.

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 will provide 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, otherwise were 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), 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 were definitely much higher than those of NBB 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 NBB 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 will add the following figure to interpret this issue more

clearly.

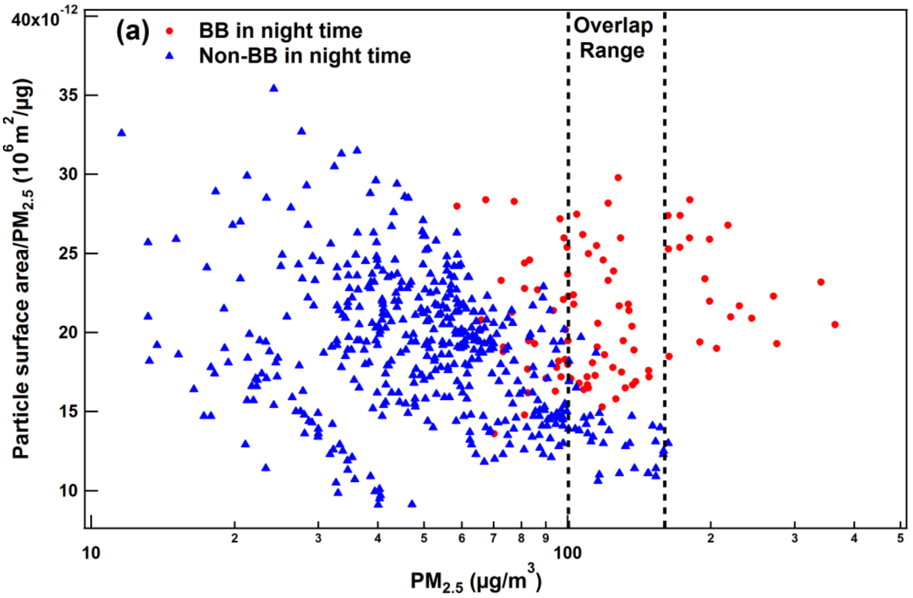

Fig. 1

In the revised manuscript, if we change the dataset to night time data, the number of data points deployed in this Figure 7 was 51 for BB samples, and 27 for NBB samples. We will add this information in the figure capture of Figure 7.

The data selection for Figure 8 was in the same case of Figure 7. 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 will add the following Fig. 2 in the revised manuscript to interpret this issue more clearly.

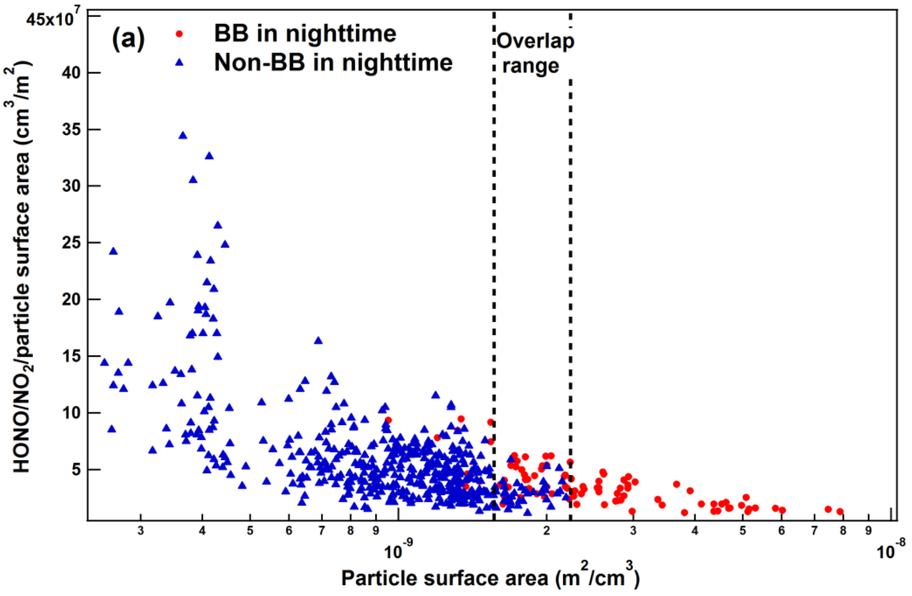

Fig. 2

In the revised manuscript, after we changed the dataset to night time data, the number of data points deployed in this Figure 8 was 35 for BB samples, and 51 for NBB samples. We will add this information in the figure capture of Figure 8.

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: Will add 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: Will change 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 will calculate the night time lifetime of HONO and add the information in the revised manuscript.

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: Will simplify 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 will add 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 will add 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 will change 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 will change the deployed dataset to the nocturnal data in Figure 5, which showed similar results.

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 will add a new sub-figure of Fig 3c to compare the nocturnal NO2 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 NBB 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 remaining ones being 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. 3b 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 will change 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 will add 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. 2b)."*

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 will calculate the ratios of nitrate to NO_y to estimate the atmospheric processing time. The results show similar values for both the June 10th event and other general BB episodes.

We will add some sentences and 2 sub-figures (new Fig. 10b and 10c) 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 will add 3 new sub-figures (new Fig. 10a-10c) 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. 10a), suggesting the further enhanced HONO concentrations during the case of 10th June were secondary 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 the plumes of 10th June were more aged than 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 showed in Fig. 10b and 10c, 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 10th 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 will add some statement on the issue in the method part.

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 will change 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 will add the samples number in the figure capture in the revised manuscript, and add a new sub-figure to interpret this issue. For the reason we chose the 100-150 $\mu g/m^3$ 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 will add the samples number in the figure capture in the revised

manuscript, and add a new sub-figure to interpret this issue. 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 will give 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 will add 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 will give the exact times of June 10 case in the revised manuscript.