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Interactive comment on "Influence of biomass burning plumes on HONO chemistry in eastern China" *by* W. Nie et al.

Anonymous Referee #1

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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.

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 μg 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 photolysis rate 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?

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?

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?

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.

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 μg 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.

Similarly, when subsequent filters (e.g. PM2.5 mass of 100 – 150 μg 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 μg 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?

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

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been shown as a potential HONO source by heterogeneous reaction of NO2 (e.g. [Bedjanian and El Zein, 2012; Langridge et al., 2009]).

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].

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?

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.

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.

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?

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?

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?

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.

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.

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.

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 μg m-3 is arbitrary. Why was this mass range selected instead of comparing the entirety of the two aerosol population measurements?

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

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.

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?

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

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?

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?

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.

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 SO2, there needs to be greater certainty that the appropriate corrections to the HONO measurement have been made.

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].

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

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

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?

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 μg 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?

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

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?

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