

Referee #3

This manuscript describes continuous ambient measurements of HONO, NO, NO₂, and PM_{2.5} at the SORPES station in Nanjing (eastern China) from November 2017 to November 2018. The main conclusions are:

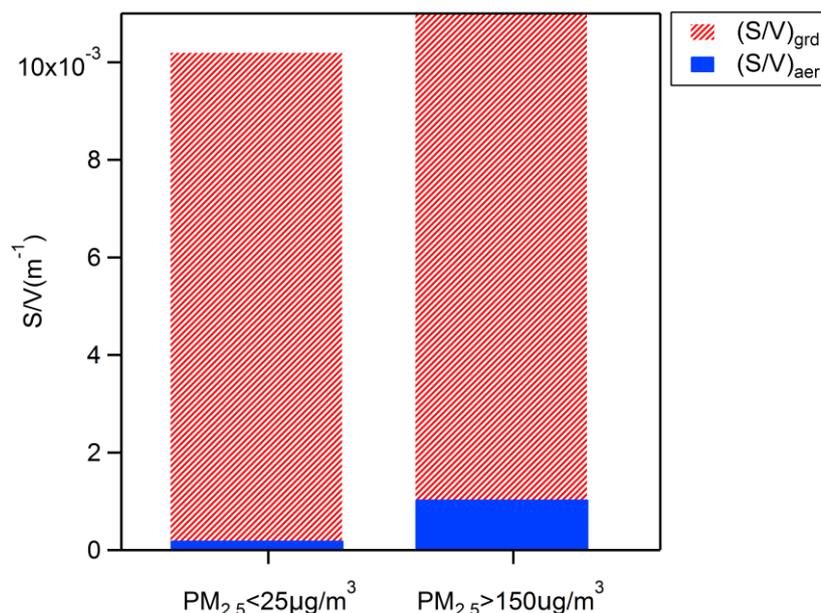
1. Seasonal average HONO concentrations are comparable to other urban/suburban regions (0.45-1.04 ppb). 2. Direct emissions from combustion sources explain nearly 25% of nocturnal HONO concentrations. The authors determined this by examining fresh plumes. 3. Nocturnal HONO formation is RH-dependent and largely explained by heterogeneous surface chemistry. 4. A missing diurnal HONO formation mechanism is a significant source of HONO around noon (average 1.13 ppb/hr).

There are not many long-term records of ambient HONO measurements, and this manuscript provides a valuable dataset to the scientific community. It is well within the scope of ACP and will likely be of interest to ACP readers. I recommend publication after the authors address the following comments.

-Figure 6 shows the HONO/NO₂ ratio as a function of RH. The authors state that Fig 6a represents measurements when available surface area is dominated by the ground (i.e., relatively low surface area contributions from aerosols). Can the authors quantify the relative contributions to total surface area from the ground and aerosols? What percentage of the total surface area does the ground represent in clean air and polluted air?

Response: Thanks for the comment and suggestion.

We calculated aerosol surface density from the particle number size distributions between 6 nm and 820 nm, by assuming that all particles are spherically shaped. and We calculated ground surface density through the equation: $(\frac{S}{V})_{\text{grd}} = \frac{1}{H}$, where H is the height of boundary layer, and a value of 100m is assumed for nighttime (Su et al., 2008). As the following figure shows, the surface area to volume ratio of ground is dominant, but under the condition of severe pollution, the aerosol can contribute about 10% of the total surface area. Besides the surface area, the conversion of NO₂ to HONO should also be determined by the surface reactivity, i.e. the uptake coefficient of NO₂-to-HONO ($\gamma_{\text{NO}_2 \rightarrow \text{HONO}}$). Differ from the prolonged exposure to oxidizing agents and radiation of the ground surface, the aerosol surface is relatively more fresh, and possibly more reactive. For example, the reduction of NO₂ in the presence of water by C–O and C–H groups in the soot is proposed to produce HONO quickly (Ammann et al., 1998). In our study, in case we assume that all of the observed HONO is formed on particle surfaces at night, the derived $\gamma_{\text{NO}_2 \rightarrow \text{HONO}}$ is 1.44×10^{-5} , within a reasonable range of laboratory measurements.



the averaged surface area to volume ratio (m^{-1}) of ground and aerosol in clean air ($\text{PM}_{2.5} < 25 \mu\text{g}/\text{m}^3$) and polluted air ($\text{PM}_{2.5} > 150 \mu\text{g}/\text{m}^3$)

Line 481-487: For 30%-100% of the measured mean C_{HONO} (0.0043 h^{-1}) in winter, the uptake coefficient of NO_2 -to-HONO ($\gamma_{\text{NO}_2 \rightarrow \text{HONO}}$) calculated from Eq. (8) is in the range of 6.9×10^{-6} to 1.44×10^{-5} , consistent with the results from many laboratory studies which demonstrate that the uptake coefficients of NO_2 (γ_{NO_2}) on multiple aerosol surfaces or wet surfaces are mainly distributed around 10^{-5} with the HONO yield varying from 0.1 to 0.9 (Grassian, 2002; Aubin and Abbatt, 2007; Khalizov et al., 2010; Han et al., 2017).

-As shown in Figure 6, HONO/NO₂ ratios in polluted air do not decline at RH between 75-95% as is seen in clean air. The authors should provide some explanation here. Why is there a different RH dependency under high PM_{2.5} conditions?

Response: Thanks for the comment and suggestion. We have added some discussion into the revised manuscript.

Line 427-438: With the increase of RH, the hygroscopic growth of aerosol particles should provide larger surface area. When RH is higher than 75%, which has exceeded the mutual deliquescence relative humidity of inorganic salts (Fountoukis and Nenes, 2007), aerosols will transfer to aqueous phase gradually, and then promoting multiphase or heterogeneous chemistry processes (Herrmann et al., 2015). For example, the oxidation of SO_2 by NO_2 on aqueous aerosol surface may produce NO_2 /HONO efficiently under polluted condition (Xie et al., 2015; Wang et al., 2016). In addition, the enhancement NO_2 uptake on micro-droplets by anions has been reported in experiments (Yabushita et al., 2009).

-The authors claim that the unknown daytime HONO production is different from the heterogeneous nocturnal production (section 3.4). It is not immediately clear how the authors reach this conclusion. They should expand on this statement and provide clear justification.

Response: Thanks for the comment and suggestion. The highest noontime P_{unknown} value is 1.72 ppb/h in spring, followed by 1.11 ppb/h in summer, 0.66 ppb/h in autumn and 0.58 ppb/h in autumn, unlike the seasonal variation of NO_2 ; and P_{unknown} shows an increase towards noon, which is also distinguished from the diurnal pattern of NO_2 . These results indicate that there must be some other factors affecting P_{unknown} , in case NO_2 is assumed to be a dominate precursor of HONO at daytime

Line 558-561: The average value of P_{unknown} normalized by NO_2 is 0.1 h^{-1} , over 18 times greater than the nighttime conversion rate (0.0055 h^{-1}), also implying that P_{unknown} cannot be explained by the nocturnal mechanism of NO_2 -to-HONO.

-A major justification for assuming an unknown HONO source is that the HONO/ NO_2 ratio rises around noon at peak solar radiation. I have two problems with this that the authors should address. First, any ratio with NO_2 in the denominator will increase as NO_2 is photolyzed at greater rates. Second – and this is the more serious concern – is that 3-D air quality models predict an increase in HONO/ NO_2 ratios in the late morning through noon, but they certainly aren't influenced by missing HONO sources (e.g. Figure 8 in <http://dx.doi.org/10.1016/j.atmosenv.2015.04.048>). While there may well be a significant unknown HONO source during the day, relying on HONO/ NO_2 ratios does not sufficiently make the case.

Response: Thanks for the comments.

For first problem, we agree that the greater rates of NO_2 can also increase the HONO/ NO_2 ratio. If just considering of the photolysis of HONO and NO_2 , both of which will convert to NO, the loss of HONO and the almost unchanged concentration of NO_x ($\text{NO}_2 + \text{NO}$) will reduce the ratio HONO/ NO_x . So we actually use the ratio HONO/ NO_x to present the conversion of NO_x to HONO partly (please see Fig.1 and Fig. 2 in the revised manuscript).

For second problem, the increase of HONO/ NO_x at daytime can result from: (1) the homogeneous reaction of NO and OH radical (R3); (2) the conversion of NO_2 to HONO (R4, R5); (3) other NO_x -independent sources. In the work of Couzo et al. (2015) (Figure 8 in <http://dx.doi.org/10.1016/j.atmosenv.2015.04.048>), when they only considered R3, the predicted daytime HONO/ NO_2 can follow the time variation of the measured ratio but underestimate significantly, and after include the heterogeneous formation from NO_2 (R4, R5) and HNO_3 (R6), the simulated HONO/ NO_2 was improved during daytime, but significantly contradicted with the observed value in the second half of the night. Until now, the heterogeneous reaction mechanisms (R4, R5, R6) are actually not clear yet, there are uncertainties involved with the parameterizations in various models, many simulation works still tend to underestimate HONO concentrations (Czader et al., 2012; Lee et al., 2016).

The missing source (P_{unknown}) defined in our study contains the heterogeneous processes mentioned above. We want to understand which mechanism might be more important based on our measurements. The source of HONO is divided into gas phase reaction (R3), combustion emission and unknown source P_{unknown} . So both the homogeneous formation and unknown source of HONO can increase the HONO/NO_x ratio at daytime, with a mean value of 0.71 ppb/h and 1.02 ppb/h, respectively. P_{unknown} has found to correlated with NO₂*UVB, indicating the photo-induced heterogeneous conversion of NO₂ to HONO, but for now we do not have any solid evidence to identify which surface (ground surface and aerosol surface) are important in this potential mechanism.

Line 534:

$$P_{\text{unknown}} = J(\text{HONO})[\text{HONO}] + k_{\text{HONO}+\text{OH}}[\text{HONO}][\text{OH}] + \frac{V_{\text{HONO}}}{H}[\text{HONO}] + \frac{\Delta\text{HONO}}{\Delta t} - k_{\text{NO}+\text{OH}}[\text{NO}][\text{OH}] - \frac{0.79\% \times \Delta\text{NO}_x}{\Delta t} \quad (10)$$

Line 261-264: If the HONO sources during daytime are consistent with those at night, the minimum HONO/NO_x ratios should occur at noon due to the intense photochemical loss of HONO. Therefore, there must be additional sources of HONO during daytime (e.g. R3).

Line 539-542: the average homogeneous reaction rate between NO and OH ($P_{\text{NO}+\text{OH}}$) is 0.71 ppb/h and P_{emis} just gives a tiny part of HONO at a rate of 0.02 ppb/h, meaning that most of HONO comes from an unknown source whose average rate (P_{unknown}) is 1.02 ppb/h, contributing about 58% of the production of HONO.

-Assuming the existence of a missing HONO source during the day, to what extent could it be explained by soil emissions?

Response: Thanks for the comment and suggestion.

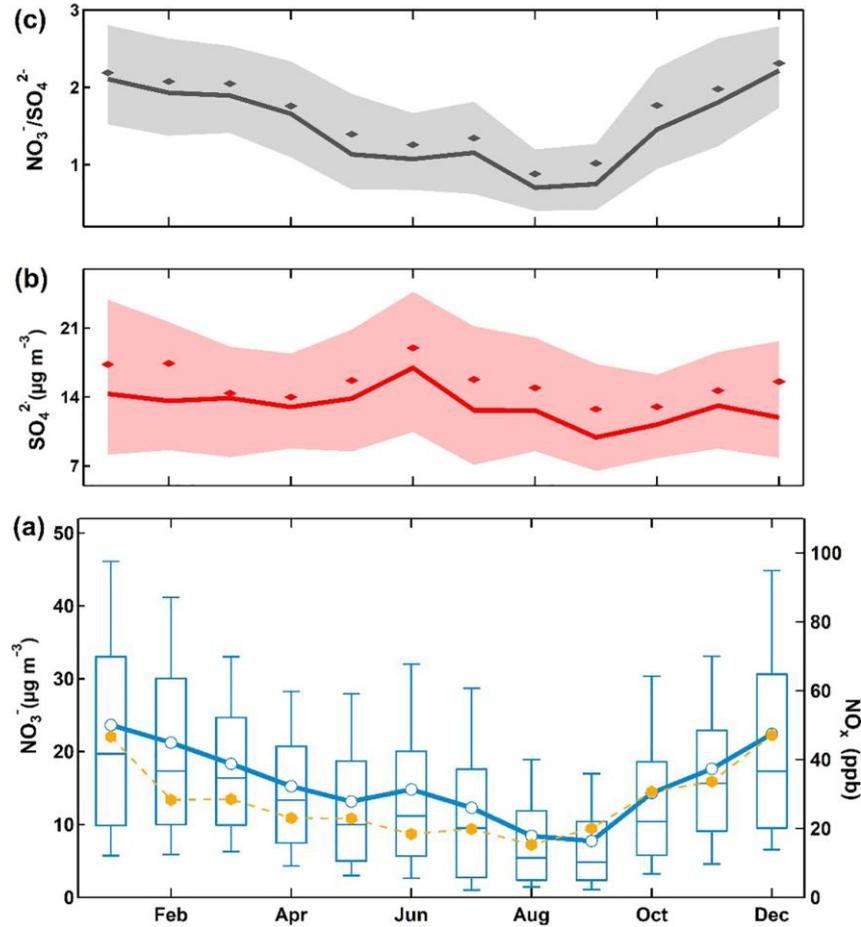
The averaged missing source calculated in our study is 1.02 ppb/h around noon (10:00-14:00 LT). So far, we cannot exclude the potential contribution from (photo-enhanced) heterogeneous reaction of NO₂, and the photolysis of adsorbed nitric acid (HNO₃) and particulate nitrate (NO₃⁻). It's difficult to derive the rate or the amount of HONO emitted from soil emission, the main reason is that we were lack of direct observation. However, we are still trying to estimate the contribution of soil emissions to HONO through solving overdetermined equations at night, due to the relatively simple sources of HONO and without the influences of HONO photolysis, and the mixing effect of boundary layer (see part 4 in the revised manuscript for details). And, in average, 14.5% of nighttime HONO is found to be explained by soil emissions. The key to our calculation is the assumption that the mixing level of observed NH₃ can represent the intensity of soil emission of HONO. Although the processes of HONO and NH₃ emission from soil may not be completely synchronized, the seasonal patterns for each should be consistent.

Line 602-614: Although we do not directly measure HONO emissions from soil, the observed ammonia can represent its monthly average intensity, based on the following hypothesis: the dominant source of NH₃ is from soil, especially from fertilizers (NH₄⁺→NH₃) for a good correlation between ammonia and temperature in the site (r=0.63, p=0.01), omitting the contributions of livestock to NH₃ since there is only a small poultry facility within 10 km of this site (Meng et al., 2011;Huang et al., 2012;Behera et al., 2013). Combustion sources (vehicles, industry, biomass burning) should contribute only a fraction of NH₃ seeing that NH₃ is not related to NO_x or CO in our study. Moreover, the release of both HONO and NH₃ depend on the strength of microbial activities, fertilizing amount, and soil properties (e.g., temperature, acidity and water content of soil). Although the processes of HONO and NH₃ emission from soil may not be completely synchronized, the seasonal patterns for each should be consistent.

-The authors state that mass concentration of PM_{2.5} is likely not the only factor affecting HONO formation on aerosol surfaces. This makes sense intuitively. Do the authors have speciated PM_{2.5} measurements during this time? How does the chemical composition of aerosols change throughout the year? Would these changes make the NO₂ to HONO conversion more or less likely?

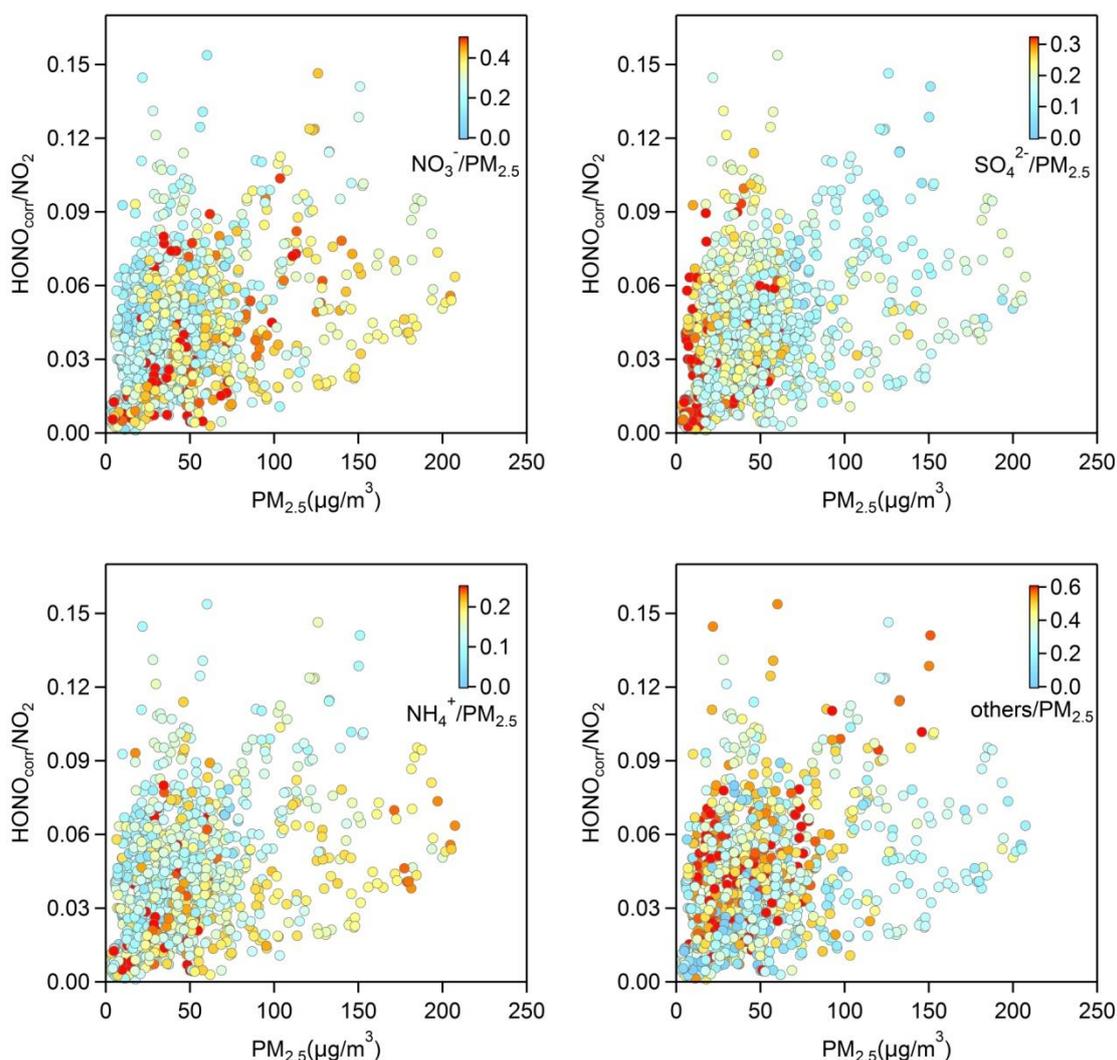
Response: Thanks for the comment and suggestion.

The seasonal variation of aerosol compositions has been reported in our previously work, showed in the following first figure: the particulate nitrate exhibits a maximum value in January and a minimum in August, and particulate sulfate shows a relatively weak seasonal cycle (Sun et al., 2018). An intuitive conclusion is that the proportion of nitrate will increase and the proportion of sulfate will decrease with the aerosol loading, from summer to winter.



Monthly averaged nitrate (blue), sulfate (red), NO_x (orange) mass concentrations and nitrate to sulfate molar-based ratio (grey) measured at the SORPES station during March 2014 to February 2016 (Sun et al., 2018).

The slope of HONO_{corr}/NO₂ and PM_{2.5} varies over a relatively wide range, caused by some unknown factors that need to be explored. As the following figure shows, when the proportion of nitrate in aerosol is higher, the slope of HONO_{corr}/NO₂ and PM_{2.5} tend to be lower slightly while the relationship shows differently for sulfate. The value of (PM_{2.5}-NO₃⁻-SO₄²⁻-NH₄⁺)/PM_{2.5} can roughly represent the ratio of organic compounds in most situations, and it seems that the high ratio of organic aerosol occurs with the high slope of HONO_{corr}/NO₂ and PM_{2.5}. But simply relying on these cannot make too much sense, for example, the heat can make particulate nitrate volatilize into nitric acid gas and cause soil to emit more HONO, so we can see the highest HONO_{corr}/NO₂ ratio and the lowest proportion of nitrate to aerosol in summer. In future work, we're going to study the impact of aerosol components to the heterogeneous formation of HONO through laboratory experiments.



Scatter plot of $\text{HONO}_{\text{corr}}/\text{NO}_2$ and $\text{PM}_{2.5}$ in the time (3:00-6:00 LT) when $\text{HONO}_{\text{corr}}/\text{NO}_2$ reaches the pseudo steady state each night and are colored by the ratios of main aerosol compositions: (a) $\text{NO}_3^-/\text{PM}_{2.5}$, (b) $\text{SO}_4^{2-}/\text{PM}_{2.5}$, (c) $\text{NH}_4^+/\text{PM}_{2.5}$, (d) $\text{others}/\text{PM}_{2.5}$, i.e. $(\text{PM}_{2.5}-\text{NO}_3^--\text{SO}_4^{2-}-\text{NH}_4^+)/\text{PM}_{2.5}$.

Other minor comments:

-Check the in-text references to Figures and Tables. Some of the Figures are mis-referenced (e.g. referencing Fig 5 when, in fact, the figure being referenced is Fig 6). This happens quite often in the latter half of the manuscript.

Response: Thanks. We have re-edited the references to Figures and Tables in the revised manuscript.

- The last sentence in the second paragraph of section 3.3.2 is particularly confusing.

Response: Thanks. We have re-edited the language in the revised manuscript.

Line 393-398: Even at the lowest measured RH of 18%, the absolute moisture content in the atmosphere is still greater than 10^3 ppm in our study, which is quite abundant to react with

NO₂, but the HONO_{corr}/NO₂ ratio is quite small and remains unchanged when RH is below 45%, indicating that the NO₂ to HONO conversion efficiency should be determined by water covering the surfaces, rather than by the amount of water in the air.

-To improve readability, try to have a native English speaker proofread the manuscript. Some of the phrases are oddly worded and obscure the authors' meaning.

Response: Thanks for the suggestion.

Reference

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