

Referee #1

This paper reports year round measurements of HONO in Nanjing, Eastern China. The effect of direct emissions of HONO is calculated by looking at fresh plumes and production of HONO from heterogeneous reaction of NO₂ on aerosol surfaces was speculated upon using nighttime HONO and RH measurements. A HONO budget was calculated, along with a missing HONO source. The effect of the measured HONO on the OH budget was also described. Understanding the role of HONO is crucial for the understanding of oxidation chemistry, especially in the urban environment therefore this study is important work that should be published. There are very few long term measurements of HONO in the literature, with most studies being done in short term campaigns. The analysis here is a reasonable attempt at understanding the role of HONO, albeit with a fairly limited set of supporting measurements. It is within scope of ACP and I recommend publication subject to completion of the following modifications.

General comments:

-No OH measurements were available during the measurements period so the authors have calculated OH concentrations for their analysis (P7). They use the work of Rohrer and Berresheim that correlates OH with J(O¹D). I find this a strange choice of literature to use as it was based on work in a very different environment. I believe there are numerous measurements of OH taken within the PRD that would be a more relevant way to infer OH concentrations for this study.

Response: Thanks for the comment and suggestion. We have reset the parameters a, b, and c, based on the OH studies in the PRD, China.

Line 190-201: The coefficient a reflects the general chemical conditions (e.g. NO_x or VOCs) at the selected place for research, and the exponent b represents the combined effects of all photolytic processes on OH, and the parameter c counts the light-independent OH sources. The values of a and b in Eq. (2) are adopted from the study in the Pearl River Delta (Lu et al., 2012). The value of c is set to 1.0×10⁶ cm⁻³, a typical nighttime OH concentration in urban areas of China (Li et al., 2012; Lu et al., 2014). The calculated OH concentrations around noon were in the range of 0.15-1.6×10⁷ cm⁻³, comparable to observations in Chinese urban atmospheres (Lu et al., 2012; Lu et al., 2013).

$$[OH] = a \times (J(O^1D) / 10^{-5} s^{-1})^b + c \quad (2)$$

(a = 5.6×10⁶ cm⁻³, b = 0.68, c = 1.0×10⁶ cm⁻³)

-The authors present a calculation of the effect of HONO on OH formation and compare it to formation by O₃ photolysis. This study needs expanding a little. OH production from the HO₂ + NO reaction would likely be the largest source in such an environment as this study. If the authors want to look at HO_x radical formation then they should also make some comment about the effect of other sources such as HCHO photolysis to form HO₂ and O₃ + alkene reactions. I realise they may not have the supporting measurements to do this accurately but some mention should be made of it.

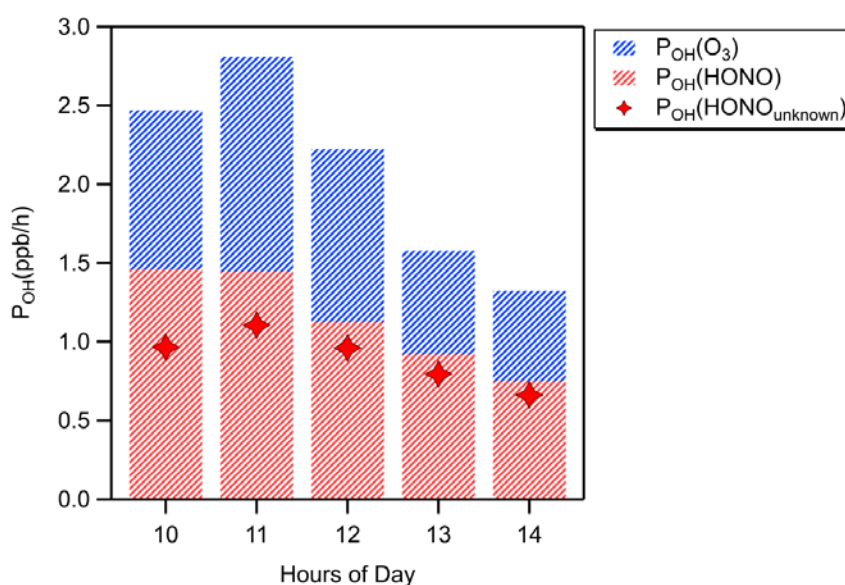
Response: Thanks for the comment and suggestion. We have added the content about the sources of OH radicals in the revised manuscript.

Line 279-285: In addition to the two mechanisms mentioned above, there are other pathways to generate primary OH radicals: the photolysis of aldehydes, especially HCHO, can form HO₂ radicals, and then react with NO to form OH radicals; the reaction of ozone with alkenes produce OH radicals directly; the ozonolysis of alkenes and nighttime reactions of NO₃ radicals with alkenes can also be net sources of OH radicals (Finlayson-Pitts and Pitts, 2000;Seinfeld and Pandis, 2016).

-Some comment should be made as to how much the ‘missing HONO’ source contributes to OH. This is important in terms of understanding how much models might be underestimating OH by not having all the HONO sources in them.

Response: Thanks for the comment and suggestion. We have quantified the relative contribution of the missing HONO source to OH in the revised manuscript.

Line 549-552: In our study, the OH production rate from the missing HONO accounts for about 78% of total P_{OH}(HONO) (Fig. S2), suggesting that the unconventional source of HONO is of significance to atmospheric oxidation.



Average OH production rates from photolysis of HONO, the missing HONO and O₃ around noon (10:00-14:00 LT), from Nov. 2017 to Nov. 2018.

-Following on from this, some mention should be made about how various air quality forecasting or regional models treat HOHO and how adding in the ‘unconventional’ sources might affect oxidation chemistry.

Response: Thanks for the comment and suggestion. We have recommended a possible mechanism that can be adopted into the models in the revised manuscript, i.e. the photo-induced heterogeneous reaction of NO₂.

Line 572-577: Our study suggest that the missing source of HONO should be considered in the air quality forecasting or regional models to characterize atmospheric oxidizing capacity better, especially in warm seasons (spring and summer). Based on the measurement (Fig. S3), the light-induced heterogeneous conversion of NO₂ to HONO on aerosol surfaces and ground surface can be included in simulation works probably, as what did in the study of Lee et al. (2016).

Minor comments:

-P5 line 150: Can the authors justify that the measurement is ‘interference free’? It was my understanding that the LOPAP instrument is subject to interference from other nitrate species. Please expand this.

Response: Thanks for the comment and suggestion. The interferences can be reduced mostly but possibly not completely by subtracting the signal of channel 2 from the signal of channel 1, so we have modified the statement in the revised manuscript

Line 143-146: In the first stripping coil, all of the HONO and a fraction of interfering substances were absorbed into solution, and the remaining interfering species (NO₂, HNO₃, PAN, etc.) were absorbed in the second stripping coil.

Line 149-151: The real HONO signal was the difference between the signals in the two channels, and the interferences can be minimized by this method.

P8 line 244: ‘in the’ should be ‘at’

Response: Thanks for the suggestion. We have corrected this in the revised manuscript.

Line 248-251: Given that the photolytic lifetime of HONO is about 10-20 min at the midday (Stutz et al., 2000), the considerable HONO concentration during daytime indicates the existence of strong production of HONO.

P9 Line 264: The authors describe HONO as an efficient reservoir of OH radicals. I’m not totally convinced this is the correct way to describe it. A reservoir suggests a long lived species that enables transport of OH radicals. I would have thought the lifetime of HONO would be very short, maybe the authors could comment on this.

Response: Thanks for the comment and suggestion. We have modified the statements in the revised manuscript.

Line 14-16: Nitrous acid (HONO), a important precursor of the hydroxyl radical (OH), has been long-standing recognized to be of significance to atmospheric chemistry, but its sources are still debate.

Line 269-270: The elevated mixing ratio of HONO presents an efficient source of OH radicals during daytime in Nanjing.

Reference

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