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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sources of nitrous acid (HONO) in the upper boundary layer and lower free troposphere of North China Plain: insights from the Mount Tai Observatory" *by* Ying Jiang et al.

Anonymous Referee #1

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The paper reports measurements of nitrous acid HONO at Mt Tai, a mountain site above the North China Plane in the Winter and Summer. The measurements were compared to the output of an MCM chemical box model to look for clues as to the processes that produce HONO values above those predicted by the NO-OH photostationary state (PSS). The measurements are interesting and their comparison to HONO measurements made at nearby surface sites are useful. I would like to see the authors expand their thinking about possible interferences in the chemical measurement, and use the MCM model to examine those. It is unfair to expect the authors to resolve these issues in this context, so I think the paper should be acceptable after some of that material is added and after the resolution of the following general and specific comments.

I have only a few specific comments/changes, and then I'd like you to consider some general issues related to using LOPAP for measuring HONO, especially in Winter.

General Comments: Wintertime HONO measurements must consider the possibility of peroxynitric acid, HO2NO2, interferences. HO2NO2 is soluble in aqueous solution and forms HONO/NO2- readily on surfaces and in aqueous solution. In addition, HO2NO2 is going to be favored at low temperatures when there is substantial HOx/NOx photochemistry (Veres et al., 2015), which is the situation at Mt Tai in the Wintertime and Springtime. There is one study that has shown the HO2NO2 interference in the LOPAP method to be about 15% (Legrand et al., 2014). However, there is at least one other data set that implies the interference could be higher than that, see the Supplemental Material of Rappenglück, et al, (2014) which describes Wintertime LOPAP measurements in the middle of an oil and gas field when intense O3 photochemical production was happening. One important piece of information in this regard is that modeling of this Wintertime photochemistry found that O3 was overpredicted by substantial amounts when the LOPAP measured HONO was used in the model compared to PSS HONO (Carter and Seinfeld, 2012).

I am not expecting the authors to resolve this issue in this work. However, since this paper has extensive MCM modeling, I would like the authors to explore several questions: What are the HO2NO2 levels predicted by their model and how do they compare to the "excess HONO? What is the O3 predicted when using both the PSS HONO and the LOPAP measured HONO and how do those levels compare to measured O3?

Modeled ozone levels that are much higher than measured would be clue that the HONO measurement has an interference. I would also note that the HO2NO2 source is HO2 + NO2, so one would expect the extra HONO (above PPS HONO) to scale with NO2 and JNO2. How does the quantity [NO2]*JNO2 correlate with PHONO?

Specific Comments:

The data used in this paper, and ideally the code used for the model, must be made

available to the community. Please deposit your data in an acceptable repository (see the ACP Instructions to Authors), or an accessible repository of your choosing. If the model code is already generally accessible, please specify where it may be obtained.

Technical Comments/Corrections

Page 1, Line 16: should be “conducted at the surface” Page 1, Line 20: Are these averages and standard deviations? Page 1, Line 21: Should be “with broad noontime maxima” Page 1, Line 29: the statement about HOx radical levels is misleading. You don’t have actual measurements of HOx radicals, only two different model cases, one based on PSS HONO and the other base on what the model says HOx would be given LOPAP measured HONO. You need to be clear about how you talk about it. When you say “underestimated” you are implying that the higher modeled HOx is in some sense “true” or “correct”, when really, it’s only a different estimate. This language is found other places in the paper and needs to be changed. Page 2, Line 9: Should be “affects human health” Page 2, Line 19: The PROPHET site is 238m in elevation, so is not a high altitude site. Page 5, Line 12: What does “SHARP” stand for? Page 6, Line 1: What are the uncertainties in the JNO2 measurements and estimates? Page 6, Line 5: What does FNL stand for? Page 6, Line 27: The definition of AOC is hard to follow based on this description. At first I thought the authors meant Sum{kOH[Xi]}, where [Xi] is the concentration of the individual species listed. That is properly termed “OH reactivity”. I think the authors mean Sum{kOH[OH][Xi]}, but they need to make that explicitly clear. Page 7, Line 22: I don’t understand what the authors mean by “inspection of data reveals the higher than expected concentration levels of HONO”. At this point in the paper, we have no context with which to judge this, i.e. we don’t know what PSS HONO is or what [HONO] at remote sites might be expected. Page 8. Line 21: It seems to me, the authors could use a tracer to more precisely determine the timing of upslope arrival at the site. Page 10, Line 1: I think there are better references for this than Donahue et al., (1973). Page 10, Line 26. The phrase the “air masses ..... facilitate a pseudo-steady state” doesn’t make sense. The short

lifetimes facilitate steady state. Page 12, Line 16: “dissected” seems like the wrong word here. I think “examined” or “explored” would be better. Page 13, Lines 20, 21: You are phrasing these results like you know what HOx and AOC is or should be, when really, you are comparing two different model results, one with and one without the additional HONO implied by the LOPAP measurements. The same kind of language is used in the Conclusions. These statements should be rephrased. Page 13, Baergen and Donaldson reference – this is a talk not a journal publication. I am fairly sure this group has a journal publication about this.

References

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Veres, P. R., J.M., R., Wild, R., Edwards, P. M., Brown, S. S., Bates, T. S., Quinn, P. K., Johnson, J. E., Zamora, R. J., and de Gouw, J. A.: Peroxynitric acid (HO2NO2) measurements during the UBWOS 2013 and 2014 studies using iodide ion chemical ionization mass spectrometry, Atmos. Chem. Phys., 15, 8101-8114., 2015.

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