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Comment on acp-2021-178

Anonymous Referee #1

Referee comment on "Budget of nitrous acid (HONO) and its impacts on atmospheric oxidation capacity at an urban site in the fall season of Guangzhou, China" by Yihang Yu et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-178-RC1, 2021

This paper presents a detailed analysis of the HONO budget in the Pearl River Delta region of China. The paper is well written, the data and the analysis are well presented. The subject is fit for publication in ACP and I would recommend the paper is accepted after the authors have addressed the following concerns.

Major Comments

1) Please add more information about the box-model. The MCM is not a model, it is just the chemical mechanism used in a model. Which software/modelling tool was used? Which VOCs were included? How was photolysis calculated for the non-measured photolysis rates? Were other processes (heterogeneous, deposition, etc..) included?

2) The molybdenum converter used to measure NOx is subject to known interferences by other NOy species. Since a large part of the analysis in this paper relies heavily on NO and NO2 data, this issue cannot be neglected. I would expect the interference to be significant under the urban conditions considered here. The authors should address this issue and examine how the results of the studies are affected by it.

3) I think the discussion in section 3.2 needs to be improved. First the observed HONO production rate should be presented and shown (how was it calculated, which are the mean values, etc..). This will make the following calculations easier to understand. Besides that, I have two main comments regarding this section.

One, the authors infer that a large missing sink of HONO is required to explain the observations (lines 274-275). However, their calculation of HONO primary emissions relies on emission inventories that are likely not very accurate. The possiiblity that HONO primary emissions are overestimated in the emission inventories cannot be neglected and needs to be discussed.

Two, the authors are deriving a primary emission rate of 0.04 ppb/h or more (line 272), a soil emission rare of 0.02 ppb/h (line 297) and a net production via OH+NO of 0.26 ppb/h (line 314), while the average observed HONO production rate is 0.02 ppb/h (line 271). From this an unknown sink of 0.25 ppb/h is inferred. First of all, in order to close the budget, the unknown sink should be 0.30 ppb/h (unless you mean that 0.05 ppb/h is lost via deposition, it is not clear from section 3.2.4). More importantly, the discussion in section 3.2.3 implies an additional, non quantified source due to NO2 reaction on surfaces. so the unknown sink is actually a lower limit (but see also the previous comment, regarding possible overestimation of primary emissions). These calculations should be make clearer, maybe with an extra "summary" subsection at the end of section 3.2.

4) In section 3.4, I would suggest that if VOC data are available, than ozonolysis of alkenes should be added here. Several studies have suggested that these process may be important in urban conditions. In fact, why not use the model results from section 3.5 to calculate the OH production pathways? It would be more comprehensive than what is shown in figure 9.

Minor Comments

lines 169-171: what does it mean that "the boundary layer diurnal cycle has been modified"? And what are the "solar altitude" and the "photolysis rate correction coefficient"?

figure 3: a blue line with pink shading is confusing. It would be better to use a shade of blue. Also why not add the results obtained with the other two methods? It may be interesting to compare them.

figure 5: I would not consider the correlation netween HONO and NO, "a good correlation". In fact it is not even linear, meaning it doesn't really provide evidence that OH+NO is a major pathway.

figure 6: can you explain why you are averaging only the top five HONO/NO2 values?