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Comment on acp-2021-178

Anonymous Referee #2

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-RC2, 2021

In this work, data collected from the Pearl River Delta in China have been used to explore potential nitrous acid (HONO) sources and their impacts on the production of hydroxyl radical (OH) and photochemical ozone (O3). The Authors perform a large number of calculations that are replicated from a variety of other publications to assess sources and sinks of HONO for their observational dataset. Despite the results of these calculations being grossly erroneous (e.g. direct emissions calculated exceeding the observations by over an order of magnitude), limited to single value comparisons (e.g. average accumulation rates calculated and observed), and using clearly erroneous assumptions (e.g. 10^6 molec cm-3 of OH at night) the Authors press on to calculate a radical budget and impact on O3 chemistry in the PRD. Overall, this work does not demonstrate any progress in our understanding of the impacts of HONO on oxidation chemistry due to fundamentally flawed data interpretation. The extreme mismatches between the calculated HONO sources and those observed are never depicted and raise serious questions regarding quality control of this work. Given that the topic of HONO sources and sinks is only the first part of this manuscript, it is not possible to consider the remainder of this work that draws on this analysis to try and improve understanding of oxidation chemistry and radical budgets. As this manuscript currently stands, it is unsuitable for publication in ACP and requires extensive re-work.

Below is an incomplete list of outstanding issues that require addressing, which may not yield an acceptable manuscript once completed, as the issues impacting this work are pervasive and beyond the scope of the requirements of peer review. The Authors are encouraged to significantly revisit the contents of the manuscript and independently ascertain that the work presents valid findings and communicates a complete understanding of the chemistry explored. As it currently stands, the manuscript replicates the prior work of others without careful reflection on whether the findings are consistent with the established knowledge of the related atmospheric chemistry.

Major issues:

- The introduction of the manuscript is unorganized and simply lists topics in nearly random order (e.g. the sources and sinks of HONO). There are basic concepts of atmospheric chemistry that do not seem to be correctly understood (e.g. microbial production of HONO is not a heterogenous reaction). There is extensive discussion of mechanisms that have been thoroughly refuted (e.g. two photon excitation of NO2 followed by reaction of the excited state with water or termolecular reactions with NH3) which are presented as topics of open debate. The Authors should significantly rework the introduction for clarity, but also with a focus on having it reflect the contents of the work being done in the manuscript. Very little text presents the outstanding issue of poor air quality and oxidation chemistry in the PRD, despite significant work having been done in this area over the past 10 years. As it currently stands, the introduction is only weakly motivating this work and can be significantly improved.
- This manuscript uses the performed HONO measurements extensively. The Authors' data is collected using a custom-built instrument that uses similar principles to the LOPAP. No prior work demonstrating the accuracy, precision, reliability through intercomparison, etc are made. Instead the Authors cite the manuscripts that established the commercial LOPAP instrumentation as though they apply to their apparatus. It is not clear if the presented QA/QC values were determined from data collected during this study or from statements others have made in the literature.
- Direct emissions of HONO calculations are grossly incorrect. The Authors present several methods from the literature that have been used previously, none of which give a reasonable result when they compare to their observations (e.g. they calculate direct emission rates of 0.3 ppbv hr-1 versus 0.02 observed). Despite having CO measurements, they do not draw on these to arrive at more reasonable estimate and belabour a number of other ways to estimate the direct HONO emission values. While one can appreciate the work done to arrive at an unexpected finding, the results conflicting with the observations in such an extreme way require some significant reflection on the state of understanding of direct HONO sources and why the established literature approaches fail to reach reasonable results with this observational dataset. Instead of taking the opportunity to make a meaningful contribution in this respect, the Authors simply press forward with further calculations on HONO sources and sinks. The absence of a temporally-resolved intercomparison between the measured and calculated direct HONO emission sources in a figure raises serious concerns. The Authors state that the site is more impacted by direct emissions than previously considered, but this result comes from a calculation that does not compare within the same order of magnitude of the observations.
- Soil emissions of HONO are not justified and rely on a set of assumptions that are not justified (e.g. boundary layer height and surrounding landscape properties) and are quite clearly in error. The HONO production rates calculated again exceed those observed significantly, raising many questions around attention to the validity of data interpretation in this manuscript.
- The use of a static OH value of 10^6 at night based on one measurement. Again, the result of the calculation differs from the observations (and again only comparing single values instead of temporally-resolved data) by over an order of magnitude.
- Deposition losses of HONO rely on reasonable production terms. Since the production terms have major errors, and this calculation propagates those, the result cannot be correct. Further considerations for this section are the large body of work that has investigated the reactive uptake coefficients for HONO on surfaces, from which dry deposition velocities can be approximated, in order to make literature comparisons that are much more recent and detailed.
- The daytime HONO budget compounds all of these errors further and the manuscript henceforth cannot be seen as scientifically reliable for further evaluation.