

Interactive comment on “Intercomparison of nitrous acid (HONO) measurement techniques in a megacity (Beijing)” by Leigh R. Crilley et al.

Anonymous Referee #2

Received and published: 21 August 2019

Review of “Intercomparison of nitrous acid (HONO) measurement techniques in a megacity (Beijing)”, AMT-2019-139 This paper presents a multi instrument comparison of HONO observations collected in Beijing. Considering the atmospheric importance of HONO, it is very important to determine the accuracy of various measurement techniques. The most refreshing part of this manuscript is that the authors make no attempts to disguise the differences between the various techniques, and do not attempt to identify a true measurement technique. This allows for a neutral consideration of the state of available technology to measure ambient HONO, while making it difficult to understand the cause of the variations. The presentation and discussion could use some work cleaning up and organizing the details of the results as it is sometimes confusing to keep track of what methods or time periods are being compared or can

C1

in fact be compared. I also find that the authors put a lot of stock in the location of sampling points as an explanation for the discrepancies, while providing limited evidence to support this. This work is valuable in that it draws attention to the continuing problem of evaluating the robustness of HONO observations. This work would benefit from attempting to arrive at a point where evidence-based suggestions can be provided to inform future observations or comparison studies. I support the publication of this work contingent upon addition minor revisions as suggested above and in the detailed comments provided below.

Page 2, line 3-4: This is oddly specific towards London considering the number of publications on daytime HONO, and that this manuscript does not address London HONO. Suggest broadening the citations for the generalization of the introduction.

Page 2, line 9: The statement “depending on the proximity to emission sources” is meant to mean what? Emission of HONO, NO_x? Direct, indirect?

Page 3, line 14: “highly polluted locations like Beijing” needs a citation or evidence otherwise that Beijing is highly polluted.

Page 4, line 3: edit to read “Measurements were performed as part of”?

Page 4, line 15: “referred to as LOPAP throughout” is a bit confusing since you just introduced that instrument will be referred to by the institution and have already defined LOPAP acronym earlier in the manuscript.

Page 4, line 25: It would be helpful in this work to explicitly discuss what the main differences between the two LOPAP techniques are.

Page 5, line 12: AIOFM is not yet defined in the text.

Page 54, line 16-21: This is pretty hard to understand here. Are you simply stating that the flow controller was not properly calibrated and describing the process to calibrate it? If so this seems like it is an unnecessary discussion as one would expect that you have calibrated your flow controllers to get accurate measurements.

C2

Page 6, line 3-4: How exactly did you consider sample loss and secondary formation of HONO in the instrument? That is not exactly the most straightforward thing to do, and it is glossed over here.

Page 6, line 24 and elsewhere: One major thing missing here that is likely very important is a detailed discussion on how the function instrument zero was determined and the associated errors involved. For example, how was the absolute error of 33ppt calculated here? Is that the variability between instrument zeros? Is once every 45 minutes sufficient to capture the variability in the background for the CIMS. Are the timescales for others important? From figure 1 it seems like incorrect background subtraction for each instrument could easily explain the difference in magnitude between the various instruments, especially considering the high degree of correlation observed. I'd really like to see a more detailed discussion of the background determination and subtraction and its impact on the reported values for each instrument.

Page 6, line 30: The lack of humidity in the dry N₂ zero should significantly impact the HONO sensitivity, you should include the humidity dependent calibration of your instrument. Does HCOOH display the same dependence? This could impact your ability to use formic acid as a surrogate to track changes in instrumental sensitivity. While this is commonly done in past studies it may not be accurate. This is also a concern for the SIFT instrument backgrounds.

Page 7, line 20: The compounds used in the relative transmission calibration curve are very different from HONO. How well is method expected to perform in approximating the HONO sensitivity considering these differences? Are the portions of a given molecule's real sensitivity that are not accurately captured by this method, for example surface losses or secondary ion chemistry, or fragmentation?

Page 7, line 24-25: This is a poorly written sentence and needs work.

Page 8, line 1-2: It is very difficult throughout this manuscript to keep track of when things overlap, how collocated sampling locations are, etc. I would really encourage

C3

the authors to come up with a better way to organize that information. Maybe a diagram would be helpful, one for summer and one for winter.

Page 8, line 27-28: you need to define what deviation in the upward or downward direction mean for CV. Is .5 better or worse than .1?

Page 9, line 9: The however doesn't seem to follow here. This isn't really a contradiction of the previous statements.

Page 10, line 5: no comma here.

Page 10, line 9: Could these observations be coupled, e.g. clean high winds from the west lower local HONO concentrations to a level that the instruments have a difficult time measuring in resulting in poorer agreement?

Page 11, line 25-26: delete "for and extended single continuous period,"

Page 11, 29-30: "This suggests the YORK instrument was measuring HONO at reasonable concentrations." What does this even mean? Do you mean to say it is accurate? Precise? How do you determine which measurement is correct to evaluate the performance of the YORK instrument?

Page 12, line 30-31: The two-channel stripping coil will only perform well if the chemical interferant is not efficiently removed in the first stripping coil. If the interference is removed efficiently in the first coil the second coil experiences a significantly lower signal and therefore does not effectively remove the signal observed in the first coil. Please consider this possibility that the two coil system is not perfect at interference removal.

Page 12, line 33: I think you are trying to make the argument here that HONO should not partition to particles because they are acidic? Do you have evidence for that at the sampling location? What about other forms of particle nitrogen that could potentially yield signal in the instrument? You say do you have any measurements to back up any of the statements that you are making here?

C4

Page 13, line 11-13: If water lowers the base line measurement compared to zero air this would impact the resulting background corrected ambient measurement. The percentage of ambient that is subtracted would large at low ambient HONO levels but would be negligible at large HONO levels. This could lead to large disagreement at low HONO levels. Yes, the calibration curve measured will only change in intercept, but the ambient data reported would be impacted.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2019-139, 2019.