Point-by-point response to review comments on manuscript acp-2021-178 "Budget of nitrous acid (HONO) at an urban site in the fall season of Guangzhou, China"

We would like to thank the reviewer for the valuable and insightful comments to improve the manuscript. We have carefully considered all the comments and revised the manuscript accordingly. In the following, please find our detailed responses to the comments of the reviewer. Referee comments are given in *black italics*, and our responses and changes in the manuscript in blue and red, respectively.

Also, we received Dr. Jörg Kleffmann's comments on this paper by email, and we have revised the manuscript accordingly. The comments and our responses are attached.

Response to Reviewer 2:

The Authors have done an excellent job revising the manuscript to reflect the state of knowledge on HONO sources and sinks, along with some analysis of its daytime sources. The extension to interpreting its impact on daytime oxidation was reasonably removed to narrow the scope of the manuscript, given the magnitude of uncertainties in the HONO analysis. The manuscript is now ready for publication in Atmospheric Chemistry and Physics, pending the following minor revisions.

Author's Response: We would like to thank the positive comments to our manuscript by the reviewer. As shown in the following, we have carefully considered all the comments and revised the manuscript accordingly.

1. Page 2, Line 50: Missing recent study by Pusede et al. (2015) that is more comprehensive than some of the works cited here for detailed explorations of formation mechanisms.

Author's Response: Thanks for the comment. We have cited Pusede et al. (2015) in Page 2, Lines 50–51 in the revised manuscript.

2. Page 2, Line 58: 'fresh air masses and vehicle exhaust' Should this be 'fresh air masses mixed with vehicle exhaust'?

Author's Response: Thanks for the comment. "fresh air masses and vehicle exhaust" has been changed to "fresh air masses mixed with vehicle exhaust" in Page 2, Line 58 in the revised manuscript.

3. Page 2, Line 61: HONO/NOx ratios throughout the depth of the nocturnal boundary layer, as well as during the day were also presented by VandenBoer et al. (2013) from the NACHTT campaign and also by a pair of papers from (Kleffmann et al., 2003; Vogel et al., 2003).

Author's Response: Thanks for the comment. We have read the papers recommended by the reviewer and cited them in Page 2, Line 62 in the revised manuscript.

4. Page 3, Lines 74-76: Here the Authors are citing HONO formation mechanisms that have been disproven in the literature, especially the excited NO2 and water vapor reaction (shown to be a two photon process, which is not atmospherically relevant). The homogeneous nucleation of NH3, NO2, and H2O has also not been found to be important because, like most atmospheric ternary reaction mechanisms, the probability of the reaction is so low that its rate of formation for HONO simply is not that important. Remove these. There is far more evidence for substantial HONO formation from heterogeneous reactions.

Author's Response: Thanks for the suggestions. We have removed the excited NO_2 and water vapor reaction, and the homogeneous nucleation of NH_3, NO_2 and H_2O in Page 3, Lines 73–75 in the revised manuscript.

5. Page 3, Line 84: 'appear to suggest' should be either 'appear' or 'suggest'. Pick one.

Author's Response: Thanks for the comment. "Vertical gradient observations appear to suggest that HONO is more likely produced from the ground surface" has been changed to "Vertical gradient observations suggest that HONO is more likely produced from the ground surface".

6. Page 3, Line 91: 'reduction on reductive' is redundant. Revise.

Author's Response: Thanks for the comment. The sentence has been changed to "HONO can also be generated by NO_2 reduction on various surfaces" in Page 3, Line 89 in the revised manuscript.

7. Page 3, Line 93: Missing the following work by (Aubin and Abbatt, 2007)

Author's Response: Thanks for the comment. We have cited Aubin and Abbatt (2007) in Page 3, Line 92 in the revised manuscript.

8. Page 5, Line 162: This is a Time-of-Flight s Mass Spectrometer. Please revise.

Author's Response: Thanks for the comment. It has been corrected in Page 5, Line 158 in the revised manuscript.

9. Page 9, Line 204: '0.2 % to 9.1 %' is here in the discussion. Maybe it would be nice to give these same values/units on panel (c) in the figure?

Author's Response: Thanks for the comment. We have corrected the units in Figure 2 panel (c) to be consistent with those in the discussion.

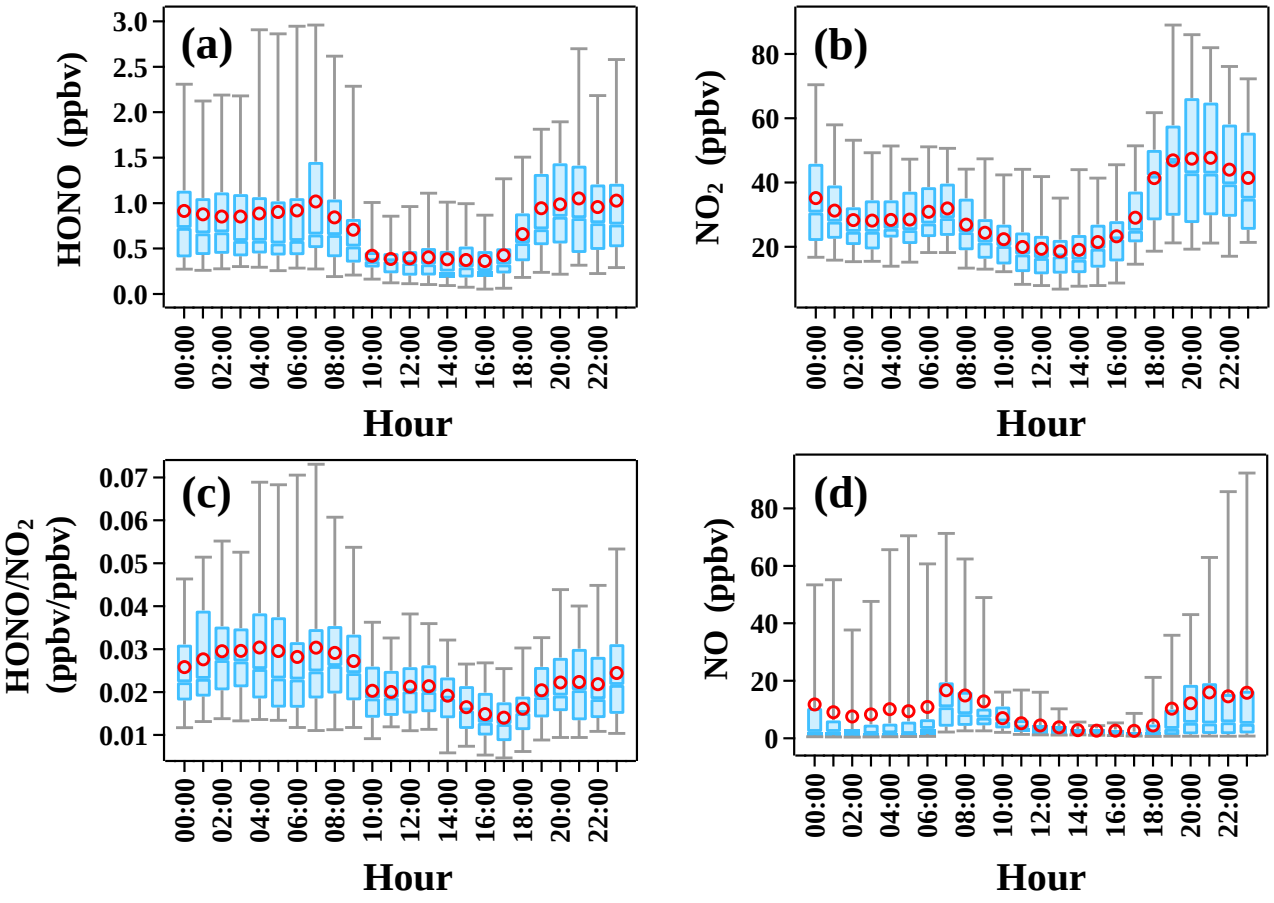

Figure 2. Diurnal profiles of (a) HONO, (b) NO_2, (c) HONO/NO_2 and (d) NO during the observation period. The blue line in the box and red circle refer to the median and mean, respectively. Upper and lower boundaries of the box represent the 75th and the 25th percentiles; the whiskers above and below each box represent the 95th and 5th percentiles. The box plots presented in this study is generated by an Igor Pro-based computer program, Histbox (Wu et al., 2018).

10. Page 10, Figure 2: The caption needs to provide reference to each panel letter in the caption text. Please add. The notation on (c) needs to be changed to more intuitive values because 0.07 or 7% are easier to interpret than 70x10^-3.

Author's Response: Thanks for the comment. As shown in the response to comment #9 above, we have provided reference to each panel in the caption text of Figure 2. In addition, the notation on (c) has been changed to more intuitive values as suggested by the reviewer.

11. Page 10, Lines 217-221: No need to letter the criteria. They are not separated and analyzed separately through a sensitivity analysis or anything later. Instead, present them in order as a list in paragraph format, with the semicolon separations retained.

Author's Response: Thanks for the comment. It has been corrected in Page 10, Lines 213–215 in the revised manuscript.

12. Page 11, Line 223: Should 'criteria' be 'all of the criteria'?

Author's Response: Thanks for the comment. "criteria (a)–(e)" has been changed to "all of the criteria" in Page 10, Line 216 in the revised manuscript.

13. Page 11, Lines 225-226: Combine the two Hong Kong studies to simplify here '… measured in Hong Kong at 1.2% (Xu et al.) and 1.0% (Yun et al.)'

Author's Response: Thanks for the comment. Two Hong Kong studies have been combined in Page 11, Lines 219–220 in the revised manuscript.

14. Page 11, Line 233: 'simply' is not needed. Remove.

Author's Response: Thanks for the comment. We have deleted "simply" in Page 11, Line 226 in the revised manuscript.

15. Page 11, Line 237: Should 'exclude' be 'estimate' or 'take into account' here?

Author's Response: Thanks for the comment. However, we believe 'exclude' makes more sense.

16. Page 12, Lines 275-276: This section is much improved and I really enjoyed reading this, following all of the motivations and comparison! Thank you!

Author's Response: We would like to thank the positive comments to our manuscript by the reviewer!

17. Page 13, Line 290: 'overall…' These are estimates. Make that clear. The alpha value above this is hard to follow through the calculation too. Why is it not presented like the other equations in the manuscript? Is the original source of this equation (Oswald et al., 2013)? Or is this equation something that is derived here? Please clarify and make a bit of a justification of why this is a valid parameterization (i.e. what has it been checked against in terms of generating a reasonable result?)

Author's Response: Eq. (5) comes from Liu et al. (2020a), and it is based on the assumption that soil HONO emission flux measured in laboratory dynamic chamber is similar to that in the field. The alpha value is just a conversion factor. HONO emission flux from grassland, F_{soil}, was calculated by a parametric formula based on experimental results from Oswald et al. (2013). We have summarized the HONO fluxes observed in field measurements in Table R1. F_{soil} (ranged from 1.0 to 3.7 ng m^{-2} s^{-1} with an average of 1.9 ± 0.6 ng m^{-2} s^{-1}) in this study is comparable to the HONO flux in grass surface (Harrison and Kitto,

1994), agricultural field (Laufs et al., 2017; Ren et al., 2011), acidic forest floor (Sörgel et al., 2015), wheat-corn field (unfertilized) (Xue et al., 2019) and rice-wheat field (Tang et al., 2020), but much lower than the HONO flux in fertilized wheat-corn field (Tang et al., 2019; Xue et al., 2019). So we think the result of soil emission through the parameterization is reasonable.

Table R1. Summary of the maximum HONO fluxes observed in field measurements (remote summit and Polar Regions were excluded).

Ground type	Research method	HONO flux ($ng\ N\ m^{-2}\ s^{-1}$)		Reference
		Min	Max	
Grass surface	Aerodynamic gradient	-7	10	(Harrison and Kitto, 1994)
		-4	7	
Agricultural field	Relaxed eddy accumulation	-4	7	(Ren et al., 2011)
Forest canopy	Relaxed eddy accumulation	-7	18	(Zhou et al., 2011)
Acidic forest floor	Aerodynamic gradient	0.1	1	(Sörgel et al., 2015)
Agricultural field	Aerodynamic gradient	0.1	2	(Laufs et al., 2017)
Wheat-corn field	Dynamic chamber system	-1	40*	(Tang et al., 2019)
Wheat-corn field	Dynamic chamber system	1	3	(Xue et al., 2019)
		6	40*	
Rice-wheat field	Dynamic chamber system	-1	8	(Tang et al., 2020)

*The measurements were conducted in a few days after fertilizer applied.

18. Page 13, Line 292: 'principle' can be deleted.

Author's Response: Thanks for the comment. We have deleted "principle" in Page 13, Line 285 in the revised manuscript.

19. Page 13, Lines 306-307: Do all of these also assume a constant nocturnal OH value? If any actually measured OH, it is worth mentioning that fact, as it lends greater support to your approximation.

Author's Response: Except that the nocturnal OH in Li et al., (2012) is a measured value, all the rest of the HONO studies in Page 13, Lines 306–307 all assume a constant nocturnal OH value. At the same time, we noticed a recent article (now under review in Atmospheric Chemistry and Physics Discussion) on the radical chemistry in the Pearl River Delta region in the autumn of 2018 (Yang et al., 2022). The averaged nocturnal OH value was reported to be around 0.4×10^6 cm^{-3} (Yang et al., 2022), which provides greater support for our approximation.

20. Page 14, Figure 3: Also missing cross-referencing of panel letters in the written caption. Please add the link between caption text and panel letters.

Author's Response: Thanks for the comment. We have added the link between caption text and panel letters in Figure 3.

Figure 3. The mean nocturnal variation of (a) P^{net}_{OH+NO}, (b) NO and (c) HONO. The blue line in the box and red circle refer to the median and mean, respectively. Upper and lower boundaries of the box represent the 75th and the 25th percentiles; the whiskers above and below each box represent the 95th and 5th percentiles.

21. Page 15, Lines 335-336: Another very nice analysis and concluding statement!

Author's Response: Again, we would like to thank the reviewer for the positive comments!

22. Page 16: Line 383: 'and uptake on aerosols' is not supported by the measurements that exist of particulate nitrite. First principles application of equilibrium thermodynamic partitioning of HONO into PM2.5 inorganic aerosol has demonstrated this is highly unfavourable (VandenBoer et al., 2014), which was show also by experiment on acidic surfaces representative of this aerosol (Kleffmann et al., 1998). The only loss to aerosol for HONO that has been shown to date, supported by sporadic measurements in the literature, is the reactive uptake of HONO on mineral carbonates in dust.

Author's Response: Our results agree well with the reviewer.

23. Page 17, Line 400: This was determined by quantitative calculation in (VandenBoer et al., 2013).

Author's Response: Thanks for the comment. We have cited VandenBoer et al. (2013) in Page 17, Lines 394–395 in the revised manuscript.

24. Page 18, Lines 429-430: Wonderful conclusion. The sensitivity analysis here is identifying exactly where improvements are required and also highlighting the complexity of this chemistry.

Author's Response: Again, we would like to thank the positive comments to our manuscript by the reviewer!

25. Page 18, Line 434: Delete 'toward'.

Author's Response: Thanks for the comment. We have deleted "toward" in Page 18, Line 428 in the revised manuscript.

26. Page 18, Line 438: Should 'unlikely more' be 'substantially less'?

Author's Response: Thanks for the comment. "unlikely more" has been changed to "substantially less" in Page 18, Line 432 in the revised manuscript.

27. Page 18, Line 439: Should 'of' be 'and'? Also, should 'largely' be 'entirely'? Since deposition is deliberately used to balance the remainder of the observations, the suggested phrasing would be more accurate. Please clarify.

Author's Response: We thank the reviewer for the constructive comments. We think "of" is more reasonable than "and". And "largely" has been changed to "entirely" in Page 18, Line 433 in the revised manuscript.

28. Page 19, Line 452: Should 'evoking' be 'exploring'?

Author's Response: We thank the reviewer for pointing out our typo. "evoking" has been changed to "exploring" in Page 19, Line 446 in the revised manuscript.

29. Page 20, Line 479: 'low wind speed' Please give the value you used to create your threshold here.

Author's Response: below 3 m s^{-1}.

Horizontal transport T_H was assumed negligible by selecting the cases with low wind speed (below 3 m s^{-1}) (Su et al., 2008; Yang et al., 2014).

30. Page 21, Line 500: 'high NOx' This is a long list. Why nothing from the polluted cities studied in North America to create a more complete global perspective? Substantial and pioneering work on HONO chemistry in high NOx areas has been done in locations such as Houston, Los Angeles, and the Uintah Basin, for example.

Author's Response: We thank the reviewer for the constructive comments. We have added references on HONO chemistry in polluted cities in North America to create a more complete global perspective as suggested by the reviewer. The original text has been revised accordingly as follows:

Apparently, high NO concentrations at our site made P_{OH+NO} the biggest daytime source of HONO, exceeding $P_{Unknown}$, similar to observations at other high-NOx sites such as the Uintah Basin (Tsai et al., 2018), Houston (Wong et al., 2013), Denver (VandenBoer et al., 2013), Santiago de Chile (Elshorbany et al., 2009), London (Heard et al., 2004), Paris (Michoud et al., 2014), Beijing (Liu et al., 2021; Slater et al., 2020; Zhang et al., 2019; Liu et al., 2020b), Hebei (Xue et al., 2020) and Taiwan (Lin et al., 2006).

31. Page 22, Figure 6: Watch the x- and y-axis formatting. They do not look consistent with those throughout the rest of the manuscript.

Author's Response: We thank the reviewer for the constructive comments. We have corrected the formatting of Figure 6 accordingly.

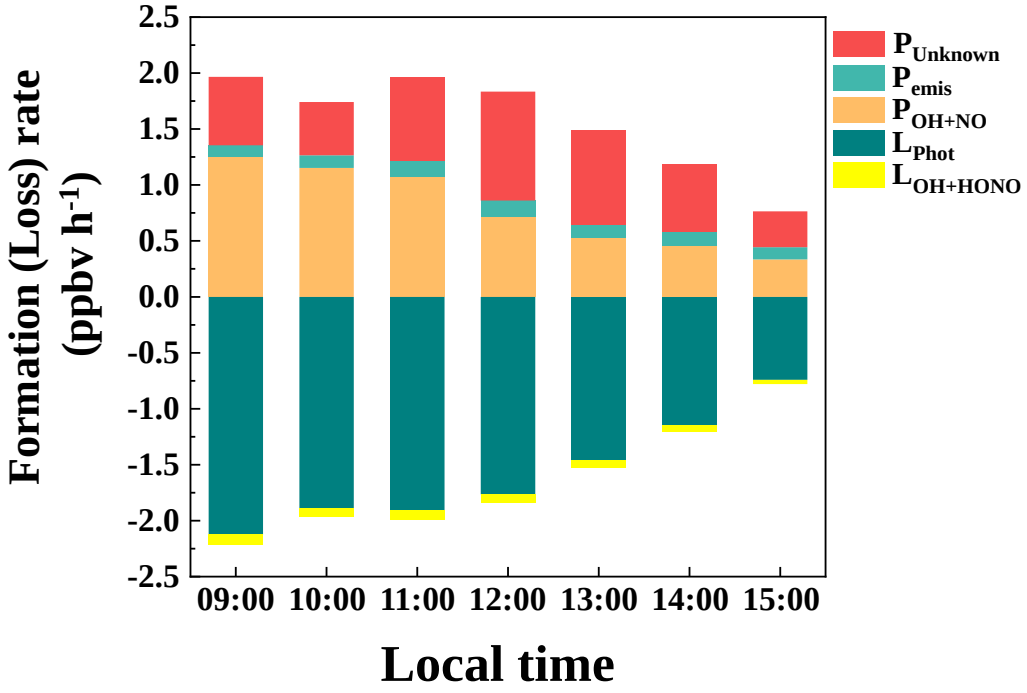

Figure 6. Items of the HONO budget (Eq. (14)) in Guangzhou during the observation period.

Minor Revisions in Supplement:

32. Page 2, Line 34: At what concentrations of nitrite was the calibration performed? And what range of HONO mixing ratios do those calibration points correspond to? Please add to improve quality of analytical description.

Author's Response: The calibration performed under 1–20 ppb sodium nitrite concentrations (corresponding to atmospheric HONO mixing ratios of 0.245–4.9 ppbv). The original text in supplement has been revised as follow:

During the instrument's operation, the instrument calibration was performed every week using the standard sodium nitrite ($NaNO_2$) solution (with the concentrations of 1–20 ppb, corresponding to

atmospheric HONO mixing ratios of 0.245–4.9 ppbv).

33. Page 2, Line 36: 'measurement' is redundant. Delete.

Author's Response: Thanks for the comment. We have deleted "measurement" it in Page 2, Line 37 in the revised supplement.

34. Page 2, Line 37: 'This 5 pptv…' This is not how precision is defined in analytical chemistry. It can be determined by the variance observed from replicate analyses of a sample (e.g. the relative standard deviation in your calibration curve slope OR the relative standard deviation of the signal from a single standard that lies in the middle of your observation range for ambient HONO). Better yet would be to present the precision at the low range of the observations and also at the high range, as these tend to be higher and lower, respectively.

Author's Response: Thanks for the comment. The precision (2σ) of the custom-build LOPAP instrument was derived from the nitrite calibration. As shown in Fig. R1, The precision (2σ) of the custom-build LOPAP is defined in this work as the minimum detectable change of a measured signal (Villena et al., 2011) and amounts to approximately 1.0% of 10 ppb nitrite concentrations (middle value of the observation range for ambient HONO). The precision (2σ) tends to be approximately 0.1% at the low range of the observations (zero air) and 4.8% at the high range of the observations (20 ppb nitrite concentrations). The original text in supplement has been revised as follow:

The precision (2σ) of the custom-build LOPAP is defined in this work as the minimum detectable change of a measured signal (Villena et al., 2011) and amounts to approximately 1.0% of 10 ppb nitrite concentrations (median value of observed ambient HONO concentrations).

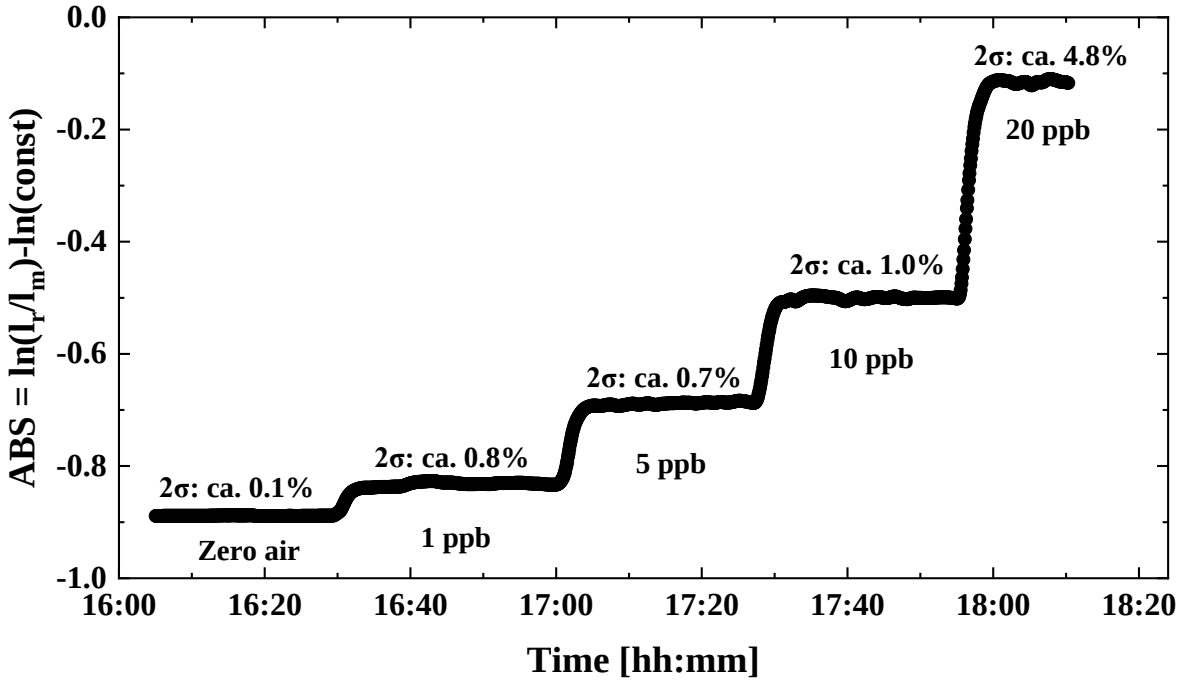

Figure R1. The precision (2σ) of the custom-build LOPAP instrument derived from the nitrite calibration (1–20 ppb) in October 15, 2018.

35. Page 2, Line 38: 'resolution' should be 'response' which is the term used below.

Author's Response: Thanks for the comment. In revised supplement Page 2, Lines 40–42 and Table S1, "resolution" has been changed to "response".

36. Page 2, Lines 47-48: The slope of the intercomparison is just as important as the correlation coefficient. Your slope suggests that the custom-build LOPAP measures systematically more HONO (~12%) than the commercial LOPAP. Did you correct your observational dataset for this? If not, you need to state this clearly in the manuscript and that it could add further uncertainty to the analysis.

Author's Response: Thanks for the comment. Putting the commercial LOPAP data on the X-axis and the custom-build LOPAP data on the Y-axis, we replotted the Fig. S2 as follow. The linear fitting line (the dashed line) has a slope of A = 1.042 ± 0.027, an intercept of B = 0.108 ± 0.022, and R^2 = 0.910 (N = 150). Such a standard correlation analysis is normally used under the conditions where the error of the x-variable is much smaller than that of the y-variable. Obviously both the errors of the x-variable and y-variable should be considered here. Thus, we further applied the "bivariate" method (Cantrell, 2008) as the reviewer suggested (the solid line in Fig. S2). The yielded slope of regression is 1.091 ± 0.026 and the intercept is 0.076 ± 0.030. The difference of the regression slope characterizes the systematic deviation for both instruments, and within the combined accuracy of them (8% and 10%). We did not correct our observational dataset because the commercial LOPAP did not work well for most of the observation period.

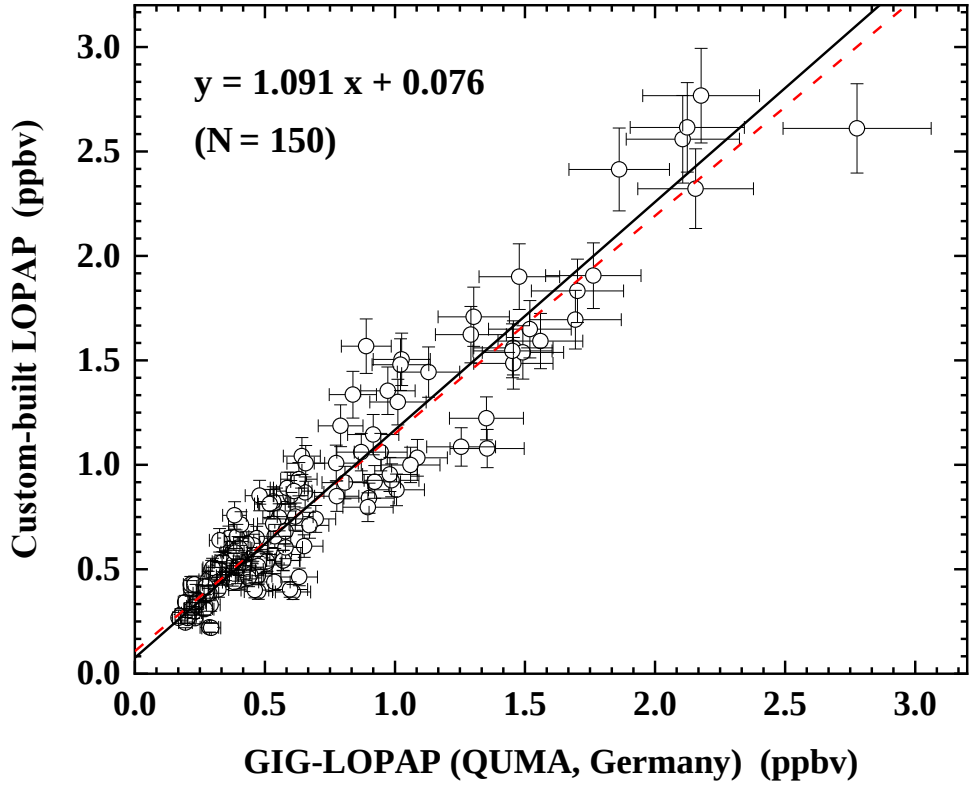

Figure S2. Intercomparison between the custom-built LOPAP with the commercial LOPAP (QUMA, Germany). The solid line denotes the linear fitting results with the "bivariate" method (slope: 1.091 ± 0.026, intercept: 0.076 ± 0.030), while the dashed line denotes that with the "standard" method (slope: 1.042 ± 0.027, intercept: 0.108 ± 0.022, R^2 = 0.910). The error bars represent the uncertainties of the custom-built LOPAP (8% + 5 pptv) and commercial LOPAP data (QUMA, Germany) (10% + 7 pptv). The HONO data from October 15–18 and November 1–6, 2018 was used for comparison.

37. Page 4, Figure S2: Is the linear fit including consideration of the uncertainties in both measurements? A standard linear regression will not return an appropriate linear equation for an intercomparison if not taken into account. If another fitting approach has been used, please give the details/name of the method used so this is clear. Also, the number of points used in the intercomparison is given as N=150, but at what time resolution is this being done? 15 minutes? That seems at odds with the 8 days stated when both

instruments were making measurements, which would yield 192 comparison points at 1 hour time resolution. Please clarify.

Author's Response: Thanks for the comment. As discussed in the response to comment #36 above, a bivariate linear regression analysis proposed by Cantrell (2008) has been applied for the intercomparison. Time resolution is 1 hour, and only 150 points within 8 days were detected by both instruments simultaneously (excluding blank check, calibration, and malfunction).

Aubin, D. G. and Abbatt, J. P. D.: Interaction of NO2 with hydrocarbon soot: Focus on HONO yield, surface modification, and mechanism, J. Phys. Chem. A, 111(28), 6263–6273, doi:10.1021/jp068884h, 2007.

Kleffmann, J., Becker, K. H. and Wiesen, P.: Heterogeneous NO2 conversion processes on acid surfaces: possible atmospheric implications, Atmos. Environ., 32(16), 2721–2729, 1998.

Kleffmann, J., Kurtenbach, R., Lörzer, J., Wiesen, P., Kalthoff, N., Vogel, B. and Vogel, H.: Measured and simulated vertical profiles of nitrous acid - Part I: Field measurements, Atmos. Environ., 37(21), 2949–2955, doi:10.1016/S1352-2310(03)00242-5, 2003.

Oswald, R., Behrendt, T., Ermel, M., Wu, D., Su, H., Cheng, Y., Breuninger, C., Moravek, A., Mougin, E., Delon, C., Loubet, B., Pommerening-Röser, A., Sörgel, M., Pöschl, U., Hoffmann, T., Andreae, M. O., Meixner, F. X. and Trebs, I.: HONO emissions from soil bacteria as a major source of atmospheric reactive nitrogen, Science (80-.)., 341(6151), 1233–1235, doi:10.1126/science.1242266, 2013.

Pusede, S. E., VandenBoer, T. C., Murphy, J. G., Markovic, M. Z., Young, C. J., Veres, P. R., Roberts, J. M., Washenfelder, R. A., Brown, S. S., Ren, X., Tsai, C., Stutz, J., Brune, W. H., Browne, E. C., Wooldridge,

P. J., Graham, A. R., Weber, R., Goldstein, A. H., Dusanter, S., Griffith, S. M., Stevens, P. S., Lefer, B. L. and Cohen, R. C.: An atmospheric constraint on the NO2 dependence of daytime near-surface nitrous acid (HONO), Environ. Sci. Technol., 49(21), 12774–12781, doi:10.1021/acs.est.5b02511, 2015.

VandenBoer, T. C., Brown, S. S., Murphy, J. G., Keene, W. C., Young, C. J., Pszenny, A. A. P., Kim, S., Warneke, C., de Gouw, J. A., Maben, J. R., Wagner, N. L., Riedel, T. P., Thornton, J. A., Wolfe, D. E., Dubé, W. P., Öztürk, F., Brock, C. A., Grossberg, N., Lefer, B., Lerner, B., Middlebrook, A. M. and Roberts, J. M.: Understanding the role of the ground surface in HONO vertical structure: High resolution vertical profiles during NACHTT-11, J. Geophys. Res. Atmos., 118(17), 10,155-10,171, doi:10.1002/jgrd.50721, 2013.

VandenBoer, T. C., Markovic, M. Z., Sanders, J. E., Ren, X., Pusede, S. E., Browne, E. C., Cohen, R. C., Zhang, L., Thomas, J., Brune, W. H. and Murphy, J. G.: Evidence for a nitrous acid (HONO) reservoir at the ground surface in Bakersfield, CA, during CalNex 2010, J. Geophys. Res. Atmos., 119, 9093–9106, doi:10.1002/2013JD020971, 2014.

Vogel, B., Vogel, H., Kleffmann, J. and Kurtenbach, R.: Measured and simulated vertical profiles of nitrous acid - Part II. Model simulations and indications for a photolytic source, Atmos. Environ., 37(21), 2957–2966, doi:10.1016/S1352-2310(03)00243-7, 2003.

Response to Dr. Jörg Kleffmann:

Dear Dr. Cheng,

With great interest I have read your recent paper Yu et al. in ACP about HONO measurements in Guangzhou to which I have a few comments. Unfortunately, I saw it only when the discussion was closed…

We would like to thank Dr. Kleffmann for the constructive comments and suggestions. The comments and our responses are given in *black italics* and blue, respectively.

1. First, good to see that you could set-up a home made LOPAP. May be as advice to improve the instruments performance, we use for R1 only 1 g/L sulfanilamide (less peaks, less crystal formation at the inlet) and only 0.1 g/l NEDA (lower reagent absorbance…) since two years. The sampling efficiency is only slightly lower (0.996 %), but reagent consumption and performance better… Did you copy that from our papers, or do you had the possibility to see an original instrument?

Author's Response: We built the LOPAP with reference to your papers, including the formulations of the solution. Many thanks to your helpful suggestion, and we will try the new formulations.

2. Line 161-162: Did you use 4 different filter radiometers because one is not sufficient for the different J-values? Or did you use a spectroradiometer (typo…)?

Author's Response: Thanks for pointing out the mistake. Actually, photolysis frequencies were measured by a spectrometer (Focused Photonics Inc., PFS-100). Detailed information can be found at this website (https://www.fpi-inc.com/product_cont_272.html). We will correct this error in the next revision.

3. Line 214 and Figure 2: Your HONO/NOx ratio may be also lower because you measured NOy and not NOx (Mo-converter in the NOx monitor…). Thus the HONO/NO2 ratios could be easily 2x higher in a photochemical active atmosphere (NOy = 2xNOx).

Author's Response: Thanks for the comment. We discussed this issue in the response of the first round as follows:

We are aware that the chemiluminescence technique combined with molybdenum converter, albeit widely used to detect NO and NO_2, suffers from the interference of some reactive nitrogen species (NOy) like HNO_3, HONO, Peroxyacetyl nitrate (PAN), other Organic nitrate, N_2O_5, etc., which can be reduced to

NO by the molybdenum converter, leading to an overestimate of NO_2 concentration. The degree of overestimation depends on both air mass age and the composition of the oxidation products/intermediates of NOx. At urban sites that are greatly affected by fresh emissions, such interference has been estimated to be 3%–10% (Xu et al., 2013; Dunlea et al., 2007**;** Villena et al., 2012), while it could be substantially higher at the suburban sites that receive aged pollution (~30–50%) (Xu et al., 2013), even up to 100% or more at some sites with the mostly aged pollution air (Dunlea et al., 2007; Steinbacher et al., 2007).

Our site is a typical urban site with heavy traffic emissions, as indicated by high concentrations of NO and NOx. Meanwhile, the average concentration of HONO, gaseous HNO_3 and particulate nitrate during the campaign were 0.74 ± 0.70 ppbv, 2.1 ± 2.0 ppbv and 4.2 ± 5.8 μg m^{-3}, respectively. PAN was not measured and is estimated around 0.84 ppbv based on earlier data at Guangzhou (Wang et al., 2015) and the other NOy species can be ignored. Based on these, we roughly estimate the relative interferences of NOz (NOy-NOx) to NO_2 to be around 10%. We think such a discrepancy would not affect the validity of our findings.

4. Section 3.2.1: I think you overestimate direct HONO emissions. If at the end of the night the HONO/NOx ratio is at least 3 % (and may be more, see above) and the peaks give only 0.9 % (see line 234, with fresh emissions NOy is low, so this number should be correct…), than the contribution of direct emissions to nighttime HONO is <30 %. But since the deposition velocity of HONO is higher than that of NO2 you lose already a lot more HONO than NO2 during night, i.e. the true HONO/NOx at the end of the night would be even higher. So I expect something like 15 %, which would agree well to former studies…

Author's Response: Thanks for the comment. We agree that 47% of the results estimated using Method (1) are too overestimated due to the limitations of this method. Nevertheless, the comparison with previous results estimated by the same method can show that direct emissions at this site is relatively high. In the latest revised manuscript we parameterized the nighttime HONO budget. The direct emissions (ranged from 0.04 ± 0.02 ppbv h^{-1} to 0.30 ± 0.15 ppbv h^{-1} with a middle value of 0.16 ± 0.07 ppbv h^{-1}) was estimated to contribute 26% to the total production rate of HONO, which is in line with our expectation.

5. Section 3.2.2: Also your nighttime HONO by NO+OH is in my view too high. You can have 10^6 OH, but not to the end of the night, where OH is typically 10^5. And especially experimental nighttime OH measured by FAGE at high VOC may be significantly too high because of known artefacts… With reasonable 10^5 you calculated 0.34 ppb integrated HONO (see Table 2). That would be lower than heterogeneously formed HONO, which I estimated from your data. If I take the slope of the HONO/NO2 ratio during nighttime shown in Figure 2c, I get a first order NO2 conversion constant ("C" in most Chinese papers) of 5x10^-7 s^-1. If I use 40 ppb NO2 (Fig. 2b) at night, I get 0.7 ppb accumulated at the end of the night, which is smaller than the 0.34 by OH+NO…

Author's Response: Thanks for the comment. There were two observations measured OH concentration in the PRD region (Hofzumahaus et al., 2009; Lu et al., 2014; Liu, 2017) in past two decades, in which the average nighttime OH concentrations were around 0.5~1.0 × 10^6 cm^{-3}. We think the data obtained from the observations at the location nearby and in the similar season are the most valuable reference. We have changed it to 0.5 × 10^6 cm^{-3} in the revised manuscript since it has caused so many concerns. 0.14 ± 0.30 ppbv h^{-1} of NO + OH reaction to HONO can be derived accordingly.

A main point of this paper is that at our site that is strongly influenced by vehicle emissions, the contributions of primary emission and consequential NO + OH reaction to HONO are higher than most previous observations. This does not rule out the heterogeneous reaction of NO_2 as a major source of HONO. In the last revised manuscript, NO_2 heterogenous reaction on ground surface (P_{ground}) and aerosol surface ($P_{aerosol}$) was estimated to be 0.27 ± 0.13 ppbv h^{-1} and 0.03 ± 0.02 ppbv h^{-1}, respectively, based on the empirical parameters in literatures. It suggests that heterogeneous reaction of NO_2 was probably the largest nighttime HONO source, despite large uncertainties.

6. Figure 6: The correlation of the HONO/NO2 with RH is always dangerous and could be an artificial one. During night the BLH decrease (increasing S/V ground…) caused by radiative cooling of the surface (T decrease). Thus also RH increase during night. Since HONO is formed on surfaces, the increasing S/V will lead to more efficient formation (which may be independent on RH…). And when the first emissions

start in the early morning, typically RH is the highest. HONO/NO2 may thus also decrease because of the fresh emission with low HONO/NOx (0.9 %) at the highest RH. Interestingly would be to see a color plot of the data with the time as color code…

Author's Response: Thanks for the comment. A color figure (Fig. R2 (a)) has been plotted as suggested, and it appears that the dots with the same color were distributed over the entire humidity range, but not concentrated in certain RH area as expected. This suggests that the correlation of the $HONO/NO_2$ with RH shown in Fig. 6 may not, at least not entirely be due to the typical distribution of RH at night. Nevertheless, we agree that the correlation of $HONO/NO_2$ with RH may not reflect the chemical characteristics of the surfaces since so many factors would play a role. We just talk about the possibilities…

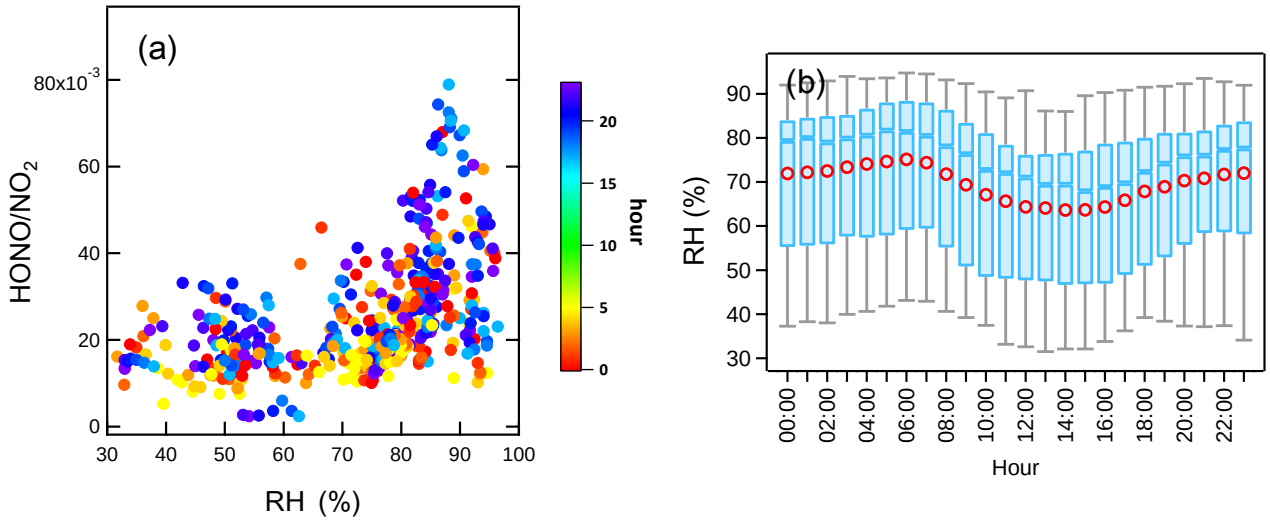

Figure R2. (a) Scatter plot of $HONO/NO_2$ ratio against RH during nighttime from 18:00 to 6:00. (b) Diurnal profile of RH during the observation period.

References

Aubin, D. G., and Abbatt, J. P. D.: Interaction of NO_2 with Hydrocarbon Soot: Focus on HONO Yield, Surface Modification, and Mechanism, The Journal of Physical Chemistry A, 111, 6263-6273, https://doi.org/10.1021/jp068884h, 2007.

Cantrell, C. A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmos. Chem. Phys., 8, 5477-5487, https://doi.org/10.5194/acp-8-5477-2008, 2008.

Dunlea, E. J., Herndon, S. C., Nelson, D. D., Volkamer, R. M., San Martini, F., Sheehy, P. M., Zahniser, M. S., Shorter, J. H., Wormhoudt, J. C., Lamb, B. K., Allwine, E. J., Gaffney, J. S., Marley, N. A., Grutter, M., Marquez, C., Blanco, S., Cardenas, B., Retama, A., Ramos

Villegas, C. R., Kolb, C. E., Molina, L. T., and Molina, M. J.: Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment, Atmos. Chem. Phys., 7, 2691-2704, https://doi.org/10.5194/acp-7-2691-2007, 2007.
Elshorbany, Y. F., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J., and Kleffmann, J.: Oxidation capacity of the city air of Santiago, Chile, Atmos. Chem. Phys., 9, 2257-2273, https://doi.org/10.5194/acp-9-2257-2009, 2009.
Harrison, R. M., and Kitto, A.-M. N.: Evidence for a surface source of atmospheric nitrous acid, Atmospheric Environment, 28, 1089-1094, https://doi.org/10.1016/1352-2310(94)90286-0, 1994.
Heard, D. E., Carpenter, L. J., Creasey, D. J., Hopkins, J. R., Lee, J. D., Lewis, A. C., Pilling, M. J., Seakins, P. W., Carslaw, N., and Emmerson, K. M.: High levels of the hydroxyl radical in the winter urban troposphere, Geophysical Research Letters, 31, https://doi.org/10.1029/2004GL020544, 2004.
Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner, A., and Zhang, Y.: Amplified Trace Gas Removal in the Troposphere, Science, 324, 1702-1704, https://doi.org/10.1126/science.1164566, 2009.
Laufs, S., Cazaunau, M., Stella, P., Kurtenbach, R., Cellier, P., Mellouki, A., Loubet, B., and Kleffmann, J.: Diurnal fluxes of HONO above a crop rotation, Atmos. Chem. Phys., 17, 6907-6923, https://doi.org/10.5194/acp-17-6907-2017, 2017.
Lin, Y.-C., Cheng, M.-T., Ting, W.-Y., and Yeh, C.-R.: Characteristics of gaseous HNO_2, HNO_3, NH_3 and particulate ammonium nitrate in an urban city of Central Taiwan, Atmospheric Environment, 40, 4725-4733, https://doi.org/10.1016/j.atmosenv.2006.04.037, 2006.
Liu, J., Liu, Z., Ma, Z., Yang, S., Yao, D., Zhao, S., Hu, B., Tang, G., Sun, J., Cheng, M., Xu, Z., and Wang, Y.: Detailed budget analysis of HONO in Beijing, China: Implication on atmosphere oxidation capacity in polluted megacity, Atmospheric Environment, 244, 117957, https://doi.org/10.1016/j.atmosenv.2020.117957, 2021.
Liu, Y.: Observations and parameterized modelling of ambient nitrous acid (HONO) in the megacity areas of the eastern China, Ph.D. thsis. College of Environmental Sciences and Engineering, Peking University, China, 2017.
Liu, Y., Ni, S., Jiang, T., Xing, S., Zhang, Y., Bao, X., Feng, Z., Fan, X., Zhang, L., and Feng, H.: Influence of Chinese New Year overlapping COVID-19 lockdown on HONO sources in Shijiazhuang, Science of The Total Environment, 745, 141025, https://doi.org/10.1016/j.scitotenv.2020.141025, 2020a.
Liu, Y., Zhang, Y., Lian, C., Yan, C., Feng, Z., Zheng, F., Fan, X., Chen, Y., Wang, W., Chu, B., Wang, Y., Cai, J., Du, W., Daellenbach, K. R., Kangasluoma, J., Bianchi, F., Kujansuu, J., Petäjä, T., Wang, X., Hu, B., Wang, Y., Ge, M., He, H., and Kulmala, M.: The promotion effect of nitrous acid on aerosol formation in wintertime in Beijing: the possible contribution of traffic-related emissions, Atmos. Chem. Phys., 20, 13023-13040, https://doi.org/10.5194/acp-20-13023-2020, 2020b.
Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Brauers, T., Oebel, A., Dlugi, R., Hu, M., Li, X., Lou, S. R., Shao, M., Zhu, T., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Nighttime observation and chemistry of HOx in the Pearl River Delta and Beijing in summer 2006, Atmos. Chem. Phys., 14, 4979-4999, https://doi.org/10.5194/acp-14-4979-2014, 2014.
Michoud, V., Colomb, A., Borbon, A., Miet, K., Beekmann, M., Camredon, M., Aumont, B., Perrier, S., Zapf, P., Siour, G., Ait-Helal, W., Afif, C., Kukui, A., Furger, M., Dupont, J. C., Haeffelin, M., and Doussin, J. F.: Study of the unknown HONO daytime source at a European suburban site during the MEGAPOLI summer and winter field campaigns, Atmos. Chem. Phys., 14, 2805-2822, https://doi.org/10.5194/acp-14-2805-2014, 2014.
Oswald, R., Behrendt, T., Ermel, M., Wu, D., Su, H., Cheng, Y., Breuninger, C., Moravek, A., Mougin, E., Delon, C., Loubet, B., Pommerening-Röser, A., Sörgel, M., Pöschl, U., Hoffmann, T., Andreae, M. O., Meixner, F. X., and Trebs, I.: HONO Emissions from Soil Bacteria as a Major Source of Atmospheric Reactive Nitrogen, Science, 341, 1233-1235, https://doi.org/10.1126/science.1242266, 2013.
Pusede, S. E., VandenBoer, T. C., Murphy, J. G., Markovic, M. Z., Young, C. J., Veres, P. R., Roberts, J. M., Washenfelder, R. A., Brown, S. S., Ren, X., Tsai, C., Stutz, J., Brune, W. H., Browne, E. C., Wooldridge, P. J., Graham, A. R., Weber, R., Goldstein, A. H., Dusanter, S., Griffith, S. M., Stevens, P. S., Lefer, B. L., and Cohen, R. C.: An Atmospheric Constraint on the NO2 Dependence of Daytime Near-Surface Nitrous Acid (HONO), Environmental Science & Technology, 49, 12774-12781, https://doi.org/10.1021/acs.est.5b02511, 2015.
Ren, X., Sanders, J. E., Rajendran, A., Weber, R. J., Goldstein, A. H., Pusede, S. E., Browne, E. C., Min, K. E., and Cohen, R. C.: A relaxed eddy accumulation system for measuring vertical fluxes of nitrous acid, Atmos. Meas. Tech., 4, 2093-2103, https://doi.org/10.5194/amt-4-2093-2011, 2011.
Slater, E. J., Whalley, L. K., Woodward-Massey, R., Ye, C., Lee, J. D., Squires, F., Hopkins, J. R., Dunmore, R. E., Shaw, M., Hamilton, J. F., Lewis, A. C., Crilley, L. R., Kramer, L., Bloss, W., Vu, T., Sun, Y., Xu, W., Yue, S., Ren, L., Acton, W. J. F., Hewitt, C. N., Wang, X., Fu, P., and Heard, D. E.: Elevated levels of OH observed in haze events during wintertime in central Beijing, Atmos. Chem. Phys., 20, 14847-14871, https://doi.org/10.5194/acp-20-14847-2020, 2020.
Sörgel, M., Trebs, I., Wu, D., and Held, A.: A comparison of measured HONO uptake and release with calculated source strengths in a heterogeneous forest environment, Atmos. Chem. Phys., 15, 9237-9251, https://doi.org/10.5194/acp-15-9237-2015, 2015.
Steinbacher, M., Zellweger, C., Schwarzenbach, B., Bugmann, S., Buchmann, B., Ordóñez, C., Prevot, A. S. H., and Hueglin, C.: Nitrogen oxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques, Journal of Geophysical Research: Atmospheres, 112, https://doi.org/10.1029/2006JD007971, 2007.

Su, H., Cheng, Y. F., Shao, M., Gao, D. F., Yu, Z. Y., Zeng, L. M., Slanina, J., Zhang, Y. H., and Wiedensohler, A.: Nitrous acid (HONO) and its daytime sources at a rural site during the 2004 PRIDE-PRD experiment in China, Journal of Geophysical Research, 113, https://doi.org/10.1029/2007JD009060, 2008.
Tang, K., Qin, M., Duan, J., Fang, W., Meng, F., Liang, S., Xie, P., Liu, J., Liu, W., Xue, C., and Mu, Y.: A dual dynamic chamber system based on IBBCEAS for measuring fluxes of nitrous acid in agricultural fields in the North China Plain, Atmospheric Environment, 196, 10-19, https://doi.org/10.1016/j.atmosenv.2018.09.059, 2019.
Tang, K., Qin, M., Fang, W., Duan, J., Meng, F., Ye, K., Zhang, H., Xie, P., Liu, J., Liu, W., Feng, Y., Huang, Y., and Ni, T.: An automated dynamic chamber system for exchange flux measurement of reactive nitrogen oxides (HONO and NOX) in farmland ecosystems of the Huaihe River Basin, China, Science of The Total Environment, 745, 140867, https://doi.org/10.1016/j.scitotenv.2020.140867, 2020.
Tsai, C., Spolaor, M., Colosimo, S. F., Pikelnaya, O., Cheung, R., Williams, E., Gilman, J. B., Lerner, B. M., Zamora, R. J., Warneke, C., Roberts, J. M., Ahmadov, R., de Gouw, J., Bates, T., Quinn, P. K., and Stutz, J.: Nitrous acid formation in a snow-free wintertime polluted rural area, Atmos. Chem. Phys., 18, 1977-1996, https://doi.org/10.5194/acp-18-1977-2018, 2018.
VandenBoer, T. C., Brown, S. S., Murphy, J. G., Keene, W. C., Young, C. J., Pszenny, A. A. P., Kim, S., Warneke, C., de Gouw, J. A., Maben, J. R., Wagner, N. L., Riedel, T. P., Thornton, J. A., Wolfe, D. E., Dubé, W. P., Öztürk, F., Brock, C. A., Grossberg, N., Lefer, B., Lerner, B., Middlebrook, A. M., and Roberts, J. M.: Understanding the role of the ground surface in HONO vertical structure: High resolution vertical profiles during NACHTT-11, Journal of Geophysical Research: Atmospheres, 118, 10,155-110,171, https://doi.org/10.1002/jgrd.50721, 2013.
Villena, G., Bejan, I., Kurtenbach, R., Wiesen, P., and Kleffmann, J.: Development of a new Long Path Absorption Photometer (LOPAP) instrument for the sensitive detection of NO₂ in the atmosphere, Atmos. Meas. Tech., 4, 1663-1676, https://doi.org/10.5194/amt-4-1663-2011, 2011.
Villena, G., Bejan, I., Kurtenbach, R., Wiesen, P., and Kleffmann, J.: Interferences of commercial NO2 instruments in the urban atmosphere and in a smog chamber, Atmos. Meas. Tech., 5, 149-159, https://doi.org/10.5194/amt-5-149-2012, 2012.
Wang, B. G., Zhu, D., Zou, Y., Wang, H., Zhou, L., Ouyang, X., Shao, H. F., and Deng, X. J.: Source analysis of peroxyacetyl nitrate (PAN) in Guangzhou, China: a yearlong observation study, Atmos. Chem. Phys. Discuss., 2015, 17093-17133, https://doi.org/10.5194/acpd-15-17093-2015, 2015.
Wong, K. W., Tsai, C., Lefer, B., Grossberg, N., and Stutz, J.: Modeling of daytime HONO vertical gradients during SHARP 2009, Atmos. Chem. Phys., 13, 3587-3601, https://doi.org/10.5194/acp-13-3587-2013, 2013.
Wu, C., Wu, D., and Yu, J. Z.: Quantifying black carbon light absorption enhancement with a novel statistical approach, Atmos. Chem. Phys., 18, 289-309, https://doi.org/10.5194/acp-18-289-2018, 2018.
Xu, Z., Wang, T., Xue, L. K., Louie, P. K. K., Luk, C. W. Y., Gao, J., Wang, S. L., Chai, F. H., and Wang, W. X.: Evaluating the uncertainties of thermal catalytic conversion in measuring atmospheric nitrogen dioxide at four differently polluted sites in China, Atmospheric Environment, 76, 221-226, https://doi.org/10.1016/j.atmosenv.2012.09.043, 2013.
Xue, C., Ye, C., Zhang, Y., Ma, Z., Liu, P., Zhang, C., Zhao, X., Liu, J., and Mu, Y.: Development and application of a twin open-top chambers method to measure soil HONO emission in the North China Plain, Science of The Total Environment, 659, 621-631, https://doi.org/10.1016/j.scitotenv.2018.12.245, 2019.
Xue, C., Zhang, C., Ye, C., Liu, P., Catoire, V., Krysztofiak, G., Chen, H., Ren, Y., Zhao, X., Wang, J., Zhang, F., Zhang, C., Zhang, J., An, J., Wang, T., Chen, J., Kleffmann, J., Mellouki, A., and Mu, Y.: HONO Budget and Its Role in Nitrate Formation in the Rural North China Plain, Environ Sci Technol, 54, 11048-11057, https://doi.org/10.1021/acs.est.0c01832, 2020.
Yang, Q., Su, H., Li, X., Cheng, Y., Lu, K., Cheng, P., Gu, J., Guo, S., Hu, M., Zeng, L., Zhu, T., and Zhang, Y.: Daytime HONO formation in the suburban area of the megacity Beijing, China, Science China Chemistry, 57, 1032-1042, https://doi.org/10.1007/s11426-013-5044-0, 2014.
Yang, X., Lu, K., Ma, X., Gao, Y., Tan, Z., Wang, H., Chen, X., Li, X., Huang, X., He, L., Tang, M., Zhu, B., Chen, S., Dong, H., Zeng, L., and Zhang, Y.: Radical chemistry in the Pearl River Delta: observations and modeling of OH and HO2 radicals in Shenzhen 2018, Atmos. Chem. Phys. Discuss., 2022, 1-19, https://doi.org/10.5194/acp-2022-113, 2022.
Zhang, W., Tong, S., Ge, M., An, J., Shi, Z., Hou, S., Xia, K., Qu, Y., Zhang, H., Chu, B., Sun, Y., and He, H.: Variations and sources of nitrous acid (HONO) during a severe pollution episode in Beijing in winter 2016, Science of The Total Environment, 648, 253-262, https://doi.org/10.1016/j.scitotenv.2018.08.133, 2019.
Zhou, X., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P. B., Carroll, M. A., Griffith, S., Dusanter, S., and Stevens, P. S.: Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, Nature Geoscience, 4, 440-443, https://doi.org/10.1038/ngeo1164, 2011.