

# Referee Report:

## Characteristics, sources, and reactions of nitrous acid during winter at an urban site in the Central Plains Economic Region in China

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### 1 Overview

The manuscript covers observations of nitrous acid (HONO) in an urban area of China during winter time. The observational data were divided into three categories according to the pollution levels marked by  $PM_{2.5}$ . Different nocturnal sources of HONO were investigated by using observational data (HONO, NO,  $NO_2$ ,  $O_3$ ) and estimated data (OH). Daytime HONO budget analysis reveals a dominant contribution to HONO production from  $NO + OH$  reaction followed by an unknown production channel. This manuscript is within the scope of ACP. I recommend that the manuscript be published in ACP after major revision.

### 2 Main comments

#### (1) 3.3. Daytime HONO budget

- (a) Line 460–461: “The  $dHONO/dt$  calculated from the measurements was small and evenly distributed around zero (Li et al., 2012)”: this sentence is directly copied from Li et al. (2012), please paraphrase.
- (b) According to Fig. 9, the values of  $dHONO/dt$  calculated in this study obviously do not show the same pattern as in Li et al. (2012). For example, the values of  $dHONO/dt$  are dominantly above zero during 10:00–13:00 local time of the PD period. It would be interesting to see a discussion on the difference between this study and Li et al. (2012).
- (c) In order to calculate the daytime budget of HONO using Eqn. (4), the chemical lifetime of HONO should be short enough (10–20 min) such that HONO is considered to be in quasi steady state (Kleffmann et al., 2005; Acker et al., 2006; Li et al., 2012). Please provide proof to show that such condition is satisfied in this study.
- (d) The values of  $dHONO/dt$  in Fig. 9 do not match the hourly HONO concentrations shown in Fig. 4 (assuming data in Fig. 4 is used to calculate  $dHONO/dt$  in Fig. 9). Take SPD period for example, the HONO concentrations are 4.4, 5.7, and 6.9 ppbv at 08:00, 09:00, and 10:00 local time, respectively. This will produce a  $dHONO/dt$  value of about 1.2 ppbv/h at 09:00 local time. However, in Fig. 9, the  $dHONO/dt$  value is at around  $-1.5$  ppbv/h at 09:00 local time of the SPD period. Please describe in detail on how the values of  $dHONO/dt$  are calculated. This

is critical since  $d\text{HONO}/dt$  is used to calculate  $P_{\text{unknown}}$ , which is discussed extensively in the daytime HONO budget section.

- (2) The writing of the manuscript generally flows in logical structure. However, there are many places where the description is a bit awkward or incorrect (see the technical corrections section). The authors should review the manuscript carefully or have it edited by a professional expert before final submission.

### 3 Minor comments

- (1) Line 88: the text states that the  $\text{H}_2\text{O}$  in R4 is isotope-labeled, please label it accordingly.
- (2) Line 119: the linked webpage shows development guidelines, please replace it with reference (with data) published in scientific journal, preferably in English, to backup the statement that Zhengzhou is an ideal place to carry out such study.
- (3) Line 156: Please provide a satellite map, either in the main text or in the supplement, to show the location of the sampling site and major pollution sources (e.g., the expressways) as mentioned in the text.
- (4) Line 179: “supplement”, please point to the specific section in the supplement.
- (5) Line 193: “The standard curve” → “The standard calibration curve”. Please specify how often was the standard calibration performed during the sampling period.
- (6) Line 195: “minimum detection limit” → “~~minimum~~ detection limit”. If “minimum” indicates that the detection limit varied significantly during the sampling period, please provide the data and discussion.
- (7) Line 221: please make sure the units are consistent for comparison in “42 ppbv (46, 63, and 78  $\mu\text{g m}^{-3}$ ”. This extends to the CO concentration comparison in the next line.
- (8) Line 380: it is not possible to draw the conclusion that “the HONO correlation in the PD period was significantly stronger” by just comparing the correlation coefficients, other factors, such as sample size, level of significance, play important rules in determining the result. Please provide details of your statistical experiment.
- (9) Line 401–402: “certain high level”, this is ambiguous, please be specific by giving the value of RH level here.

### 4 Technical corrections

- (1) Line 89: “have concentrated on” → “have been focused on”.
- (2) Line 117–118: “CPER is the important region for food production and modern agriculture published by the Chinese government” → “CPER is an important region for food production and modern agriculture according to data published by the Chinese government”.

- (3) Line 172: “5.5 mM” → “5.5 mol m<sup>-3</sup>”. Please use SI unit. Please provide the manufacturer of H<sub>2</sub>O<sub>2</sub> if this information is available.
- (4) Line 181: “A temporal” → “The temporal”.
- (5) Line 187: “were subjected to” → “were subject to”.
- (6) Line 215: “mean value ± standard deviation” → “mean value ± 1 standard deviation”. Please update all the other such occurrences in the text.
- (7) Line 279: “molecule cm<sup>-3</sup>” → “cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>”.
- (8) Line 280: “[OH] is the concentration of OH that was not measured during the campaign.” → “The concentration of OH was not measured during this campaign.”
- (9) Line 281: “Therefore, ” → “~~Therefore,~~”.
- (10) Line 289: “the reaction rates of k<sub>OH+NO</sub> and k<sub>OH+HONO</sub>” → “the values of k<sub>OH+NO</sub> and k<sub>OH+HONO</sub>”.
- (11) Line 291–292: “The error bars of Fig. 5 were placed separately in the tables of the supplement (Table S3).” → “The uncertainties of P<sub>OH+NO</sub><sup>net</sup>, NO, and HONO in Fig. 5 are shown in Table S3.”. Please revise similar description in line 418–419.
- (12) Line 295–297: “We assumed ±50% OH values to estimate the uncertainty of P<sub>OH+NO</sub><sup>net</sup>. The OH values of 1.25 × 10<sup>5</sup> and 3.75 × 10<sup>5</sup> molecule cm<sup>-3</sup> were calculated the P<sub>OH+NO</sub><sup>net</sup> values of 0.16 and 0.49 ppbv h<sup>-1</sup>” → “The uncertainty of P<sub>OH+NO</sub><sup>net</sup> is calculated based on an assumed uncertainty of ±50% in OH concentration”.
- (13) Line 357: “the 6.2% average” → “the averaged value of 6.2%”.
- (14) Line 375: “occupied an important position” → “played an important rule”.
- (15) Line 397: “influenced” → “influences”.
- (16) Line 424: please revise the broken sentence “relatively s In the current study, directly emitted HONO state (Stutz, 2002)”.
- (17) Line 455: “ΔHONO/Δdt” → “ΔHONO/Δt”

## References

- Acker, K., Möller, D., Wieprecht, W., Meixner, F. X., Bohn, B., Gilge, S., Plass-Dülmer, C., and Berresheim, H.: Strong daytime production of OH from HNO<sub>2</sub> at a rural mountain site, *Geophysical Research Letters*, 33, <https://doi.org/10.1029/2005GL024643>, <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2005GL024643>, 2006.
- Kleffmann, J., Gavriloaiei, T., Hofzumahaus, A., Holland, F., Koppmann, R., Rupp, L., Schlosser, E., Siese, M., and Wahner, A.: Daytime formation of nitrous acid: A major source of OH radicals in a forest, *Geophysical Research Letters*, 32, <https://doi.org/10.1029/2005GL022524>, <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2005GL022524>, 2005.
- Li, X., Brauers, T., Häseler, R., Bohn, B., Fuchs, H., Hofzumahaus, A., Holland, F., Lou, S., Lu, K. D., Rohrer, F., Hu, M., Zeng, L. M., Zhang, Y. H., Garland, R. M., Su, H., Nowak, A., Wiedensohler, A., Takegawa, N., Shao, M., and Wahner, A.: Exploring the atmospheric chemistry of nitrous acid (HONO) at a rural site in Southern China, *Atmospheric Chemistry and Physics*, 12, 1497–1513, <https://doi.org/10.5194/acp-12-1497-2012>, <https://www.atmos-chem-phys.net/12/1497/2012/>, 2012.