

Manuscript title: Characteristics, sources and reactions of nitrous acid during winter in the core city of the Central Plains Economic Region in China via high-time-resolution online measurements

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Hao et al. present measurements of nitrous acid using ambient ion monitor as well as HONO budget during January 2019 in Zhengzhou (China). After a very brief description of the experiment and of the measurements of HONO and other compounds (see 1st main comment), the authors classified the campaign into three periods regarding the level of pollution using PM_{2.5} measurements as a parameter for the classification: clean days (CD), pollution days (PD) and severe pollution days (SPD). They then discuss the level of HONO as well as the nocturnal and daytime budget of HONO for these different time period. This reveals high concentrations of HONO for the whole campaign with increasing concentrations while the level of pollution increases. This study also highlights the low contribution of heterogeneous NO₂ conversion to the nocturnal HONO budget while the net homogeneous production of HONO at night may have been the main factor for the increase in HONO under high NO_x conditions, even if this conclusion may be revised due to wrong level of OH used in the calculation (see 2nd main comment). In addition, the authors estimate the unknown source of HONO during the three periods revealing important level of missing sources for HONO which increase with the level of pollution. The authors, therefore, point out that further research is needed to identify these missing processes but do not try to give some insight in the identification of these processes (see 4th main comment). In conclusion, this manuscript is within the scope of ACP and will be of interest for the atmospheric community. I therefore recommend publication in ACP but after major revision.

Main comments:

1) The description of HONO measurements is too brief and insufficient while all the study rely on it. A detailed and self-sufficient description of the measurement technique for HONO is therefore needed even if it has been described in another study. Estimation of instrumental uncertainties are also lacking.

Furthermore, description of the measurement techniques used for ancillary species should also be given (at least the measurement principle and not only the model and brand of the analyzers).

On the contrary Fig. S1 and S2 does not bring valuable information and should be completed to describe more precisely the measurement principle or should be removed.

2) P10, line 253: 1.0×10^6 molecules cm⁻³ is very high for nighttime concentrations of OH especially in January. Lelieveld et al. (2016) report nocturnal concentrations of OH between 1.5×10^4 and 3×10^4 molecules cm⁻³ for January in the region concerned by the present study

and not 1.0×10^6 molecules cm^{-3} as stated by the authors. Tan et al. (2018) also found nighttime OH concentrations below 1×10^5 in Beijing during winter (February). The calculation of $P^{\text{net}}_{\text{OH}+\text{NO}}$ should therefore be corrected using a more realistic OH concentrations. This may change the quantitative and relative contribution of homogeneous reaction to accumulated HONO formation at night. In this case, discussion and conclusion of the article on this point should also be revised consequently.

3) A restructuration of section 3.3 is needed. Indeed all the paragraphs between the beginning of this section and the introductive paragraph for equations 4 to 6 (i.e. from P15, line 402 to P16, line 432) should be moved after these equations (i.e. eq. 4 to 6). Indeed, these paragraphs described the different terms used in the equation 4, 5 and 6 while they do not have been presented yet and this make the reading of this section very confusing.

4) P15, lines 403-404: “ P_{unknown} is the production rate by an unknown daytime HONO source”. Please explain how P_{unknown} is calculated. Do you assume that $d\text{HONO}/dt$ is equal to zero to do so? If it is the case, it should be indicated somewhere.

P17, lines 459-460: “However, further research is needed to analyze the unknown sources of daytime HONO”.

Why didn't you do it in this study? A deeper analysis of the processes that may be responsible for the observed unknown HONO production would have been valuable in this study. This further analysis is missing to strengthen the interest of this study for publication.

Minor comments:

-P1, line 22: Change “(i.e., the concentration of NO...” for “(i.e., when the concentration of NO...”.

-P2, line 32: Change “The hourly abatement level of HONO abatement” for “The hourly level of HONO abatement”.

-P2, line 46: Change “OH radical is also an important oxidant” for “OH radical is an important oxidant”.

-P2, lines 49-50: "Therefore, reaction changes during pollution can be observed by studying the formation mechanism of HONO".

This sentence is not clear to me. Please clarify it or remove it.

-P2, lines 53-54: "Nitro-Mac" is the name of the instrument but it does not describe the technique of measurement. Please replace it by "wet chemical derivatization technique-HPLC/UV-VIS detection".

-P3, line 55: The description of instruments existing for HONO measurements is not exhaustive. Important techniques such as IBBCEAS (e.g. Min et al., 2016; Duan et al., 2018) or CIMS (e.g. Hirokawa et al., 2009 ; Roberts et al., 2010) are missing. Please add them to your list.

-P3, line 72: Change "be absorbed by" for "react with".

-P5, lines 137-138: "The site is close to the West Fourth Ring Road".

How far is it? Please be more precise.

-P6, line 142: "High-Time-resolution instrument".

A temporal resolution of 1h is not what is usually called high time resolution. Please change the title of this section.

-P6, line 153: Change "(e.g., O and N)" for "(e.g., O₂ and N₂)"

-P7, lines 166-168: "The instrument parts and consumables should be changed regularly during the observation process, and the sampling flow should be calibrated to reduce the negative effect of accessories on sampling".

Could you be more specific? How often these maintenances have been made during the measurement period? What consumables exactly have been changed?

-P7, lines 169-170: “the denuder was replaced every six weeks. Standard anion and cation solutions were prepared every two months”.

The measurement period lasted only three weeks from 9 to 31 January 2019. How is it compatible with the frequency of replacement given here and the frequency of calibration? Please clarify.

-P7, line 192: Wind direction is not presented in table 2. Please remove it from the list of parameters presented in table 2.

-P8, line 217: Change “Fig. S3” for “Fig. 3”.

The comparison of diurnal variation of HONO during the three period is given in Fig. 3 and not in Fig. S3. Fig. S3 concerns the whole measurement period. Once the modification will be made, there will be no reference in the article to Fig. S3. So please comment this figure in the text or remove it from the supplement.

-P8, lines 217-218: “The NO and NO₂ concentration increased in the morning rush hours, decreased rapidly afterward, and remained low in the afternoon.”

This statement is not true for NO₂ and only right for NO during the CD period but not for the PD and SPD period. Please modify this statement consequently.

-P10, line 251: Change “that cannot be obtained in the measurement” for “that was not measured during the campaign”.

-P10, line 253: Wrong unit: please change “cm³ molecule⁻¹” for “molecule cm⁻³”.

-P11, line 279: Change “the hourly abatement level of HONO abatement” for “the hourly level of HONO abatement”.

-P11, lines 278-282: “Second, the hourly abatement level of HONO abatement pathways, except OH + HONO, should be at least 1.47 ppbv h⁻¹ (i.e., 13.41 - 1.59 ppbv) / 8 h). The

contributions of other HONO abatement pathways in the current work even exceeded the formation of heterogeneous reactions, similar to a previous study (Spataro et al., 2013).”

If this statement is maintained after the recalculation of $P_{\text{OH+NO}}^{\text{net}}$ using a more realistic nocturnal OH concentrations, authors should comment on which other losses of HONO can be significant at night (e.g. deposition, heterogeneous losses...). At least, a raw estimation of loss by deposition could be performed to estimate whether it can explain the lacking abatement processes.

-P13, lines 342-344: “The increased HONO in ambient air during the pollution period could have been caused by the comparatively high loading and large particle surface”.

The fair correlation between HONO concentrations and $\text{PM}_{2.5}$ mass concentrations may also just pinpoint the mainly anthropogenic origins of these two pollutants with high direct or indirect contribution of combustion sources for both of them and not the importance of HONO heterogeneous formation pathways on aerosol surfaces. A correlation between the calculated unknown source of HONO and the $\text{PM}_{2.5}$ mass concentrations (as a proxy for aerosol surface even if it is not perfect) would have been more convincing. Authors can probably use the P_{unknown} calculated in section 3.3 to perform this correlation.

-P14, line 383: Change “in then current study” for “in the current study”.

-P15, line 393: Change “the conversion rates” for “the averaged conversion rates”.

-P15, lines 395-396: Change “The improvement” for “the increase”.

-P15, lines 398-399: “the high utilization efficiency of the aerosol surface due to good particle surface properties”.

I do not understand this statement. Please clarify and rephrase.

-P15-16, lines 415-418: “the tropospheric ultraviolet and visible (TUV) transfer model of the National Center for Atmospheric Research (http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/) (Hou et al.,2016) was used to calculate the J_{HONO} value”.

It should be addressed that the J_{HONO} values obtained this way are only suitable for clear sky days without clouds, unless the presence of clouds have been taken into account. If so, the method used should be described. Furthermore, the values for O_3 column as well as for the surface albedo used in TUV model should be indicated and justification about the choice of these values should be given.

-P16, lines 418-419: “The concentration of OH radicals was calculated with the formulas of NO_2 , O_3 , and JO^1D ”.

Please specify the equation used for OH calculation.

-P16, line 427: “The mean values of J_{HONO} and OH radical concentration”.

Is it daily mean or mean values at noon? Please specify this.

-P17, lines 454-455: “Although the values of $P_{\text{OH+NO}}$ had high uncertainty because of the NO concentrations”.

How NO concentrations can affect largely the uncertainties of $P_{\text{OH+NO}}$ calculations? Does NO measurements suffer from high uncertainties? Why? If this is the case this point should be also addressed in the section 2.2. Please clarify this statement.

-Fig. 8: Please modify the legend of the figure to be consistent with the title and the manuscript (use PD and SPD instead of HD and SHD). Furthermore, J_{HONO} and JO^1D are shown only for two periods and not for all three. Why? Please include the values for the third period (SPD) or explain why it is not shown.

-Table 2: Please remove WD from the title of the table since no data of wind direction is shown in it.

Reference:

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