
Itemized Response to Anonymous Referee #2's Comments

Ms. Ref. No.: acp-2019-916

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

Response to Anonymous Referee #2:

We have carefully addressed your comments on our manuscript and made necessary revisions of the previous manuscript. We sincerely thank you for valuable and constructive inputs. We believe that we have adequately addressed all of your comments and thus the current version has been greatly improved with those valuable comments and further English editing. The revised phrases/sentences/paragraphs are shown in the line number of the revised text.

The followings are our itemized replies to your comments.

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.

Response: Thank you for your comment. A detailed description of this inlet design and the performance characteristics of the AIM system can be found in Markovic et al. (2012). HONO was hygroscopically grown in the parallel plate denuder and collected as an aqueous solution in a cyclone assembly. The aqueous sample

aliquots from both channels were transported to the ion chromatographic systems housed inside a ground container for hourly semicontinuous online analysis of HONO. The ion chromatographic system was calibrated for NO_2^- using mixed anion standard solutions of NO_2^- , which was concentrated and analyzed as described by Markovic et al. (2012).

So, we have modified the sentence in the revised text.

L 176-179: This measurement method and its details have been successfully evaluated in many field studies (Markovic et al., 2012; Tian et al., 2018; Wang et al., 2019), and shown in the supplement.

In the supplement, we have added, this part in the supplement.

1. This AIM method and its details.

HONO was hygroscopically grown in the parallel plate denuder and collected as an aqueous solution in a cyclone assembly. The aqueous sample aliquots from both channels were transported to the ion chromatographic systems housed inside a ground container for hourly semicontinuous online analysis of HONO. The ion chromatographic system was calibrated for NO_2^- using mixed anion standard solutions of NO_2^- .

The description of the measurement techniques and instrumental uncertainties was shown in **Table S1**.

Table S1. Measured species and performance of the instruments.

Species	Measurement technique	Detection limit	Accuracy
$\text{PM}_{2.5}$	Tapered Element Oscillating Microbalance	$1.5 \mu\text{g m}^{-3}$	$\pm 5\%$
HONO	Ion Chromatography	4 pptv	$\pm 20\%$
CO	Absorbs Infrared Radiation	40 ppbv	$\pm 5\%$
NO	Chemiluminescence	60 pptv	$\pm 20\%$
NO_2	Chemiluminescence	300 pptv	$\pm 20\%$
O_3	UV photometry	0.5 ppbv	$\pm 5\%$

The results came from instrument manufacturers.

At last, Fig. S1 and S2 have been 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).

Response: Thank you. Your comment is critical and important. We revisit and determine the OH concentration. You are right. $2.5 \times 10^5 \text{ cm}^3 \text{ molecule}^{-1}$ is very high for nighttime concentrations of OH, especially in January.

And, nighttime OH concentration increased as the latitude decreases ranged 3 to $6 \times 10^5 \text{ cm}^3 \text{ molecule}^{-1}$ (Lelieveld et al., 2016) (On the first figure) by the general circulation model EMAC (ECHAM/MESSy Atmospheric Chemistry).

Tan et al. (2018) found that by the field measurement, the average concentration of $\cdot\text{OH}$ in Beijing at nighttime was about $2.5 \times 10^5 \text{ cm}^3 \text{ molecule}^{-1}$ (On the second figure). There is no specific concentration of $\cdot\text{OH}$ at nighttime in winter in the study (Tan et al., 2018).

Moreover, the same $\cdot\text{OH}$ concentration ($2.5 \times 10^5 \text{ cm}^3 \text{ molecule}^{-1}$) was also used to calculate the homogeneous reaction of HONO in the recent research (Zhang et al., 2019). And, nighttime OH concentration increased as the latitude decreases ranged 3 to $6 \times 10^5 \text{ molecule cm}^{-3}$ (Lelieveld et al., 2016). Zhengzhou has a lower latitude than Beijing, so the concentration of OH used in this study is $2.5 \times 10^5 \text{ cm}^3 \text{ molecule}^{-1}$.

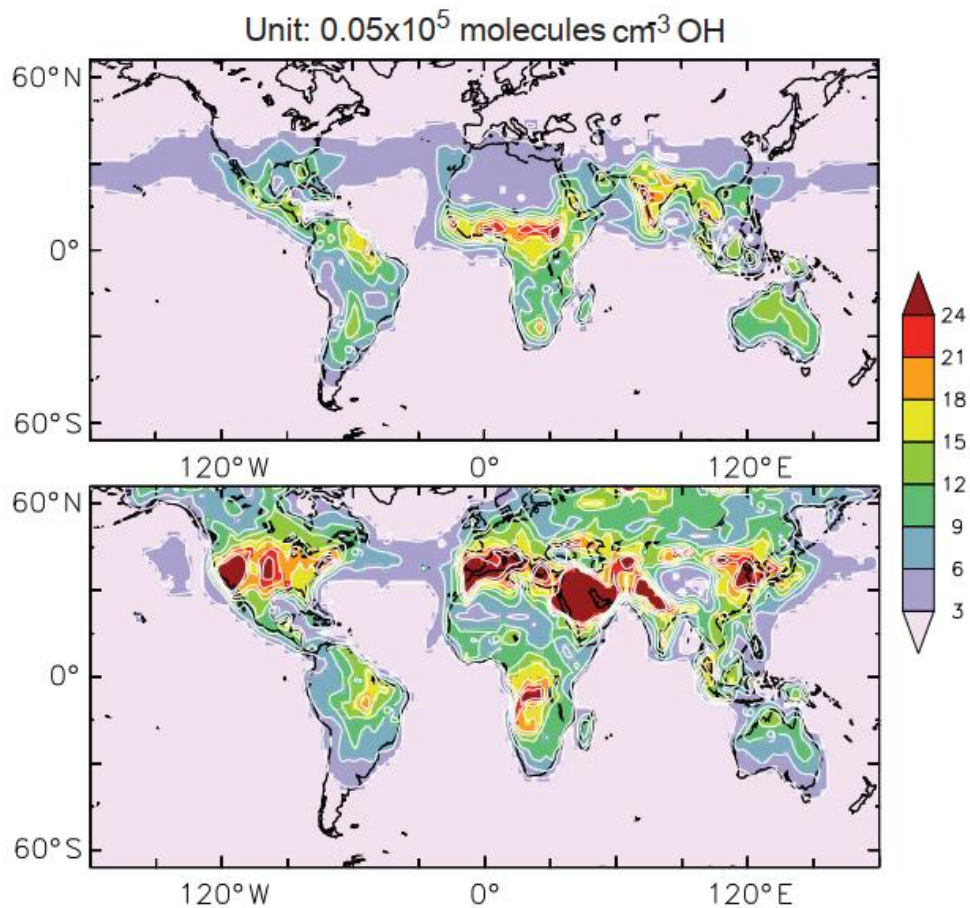


Figure 2. Nighttime OH in the boundary layer in January (top) and July (bottom). Color coding is the same as Fig. 1, but concentrations are scaled by a factor of 20 ($\times 0.05 \times 10^5$ molecules cm^{-3}).

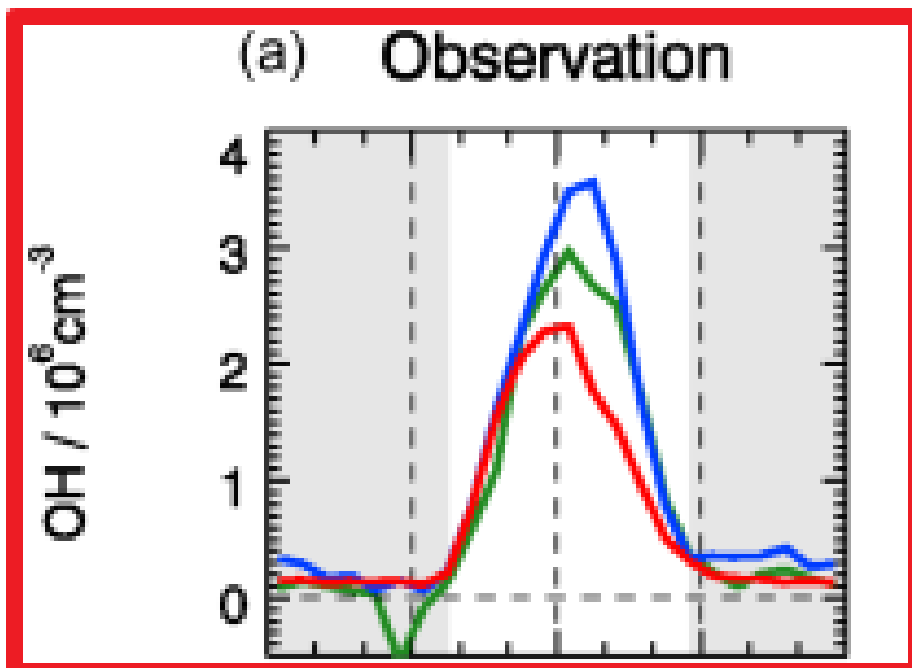


Figure 7. Mean diurnal profiles of observed (a) and modeled (b) OH, HO₂, RO₂, and k_{OH} for three different chemical and meteorological conditions. The categories for background, clean, and polluted episodes are the same as in Table 2, and similar to those applied to Figs. 9 and 12. The grey areas denote nighttime.

So, we have modified the sentences in the revised text.

L 281-288: Therefore, Tan et al. (2018) found that by the field measurement, the average concentration of ·OH in Beijing at nighttime was about 2.5×10^5 molecule cm^{-3} . Moreover, the same ·OH was also used to calculate the homogeneous reaction of HONO in the recent research (Zhang et al., 2019). And, nighttime OH concentration increased as the latitude decreases ranged 3 to 6×10^5 molecule cm^{-3} (Lelieveld et al., 2016). Zhengzhou has a lower latitude than Beijing, so the concentration of OH used in this study is 2.5×10^5 molecule cm^{-3} .

The calculation of $P_{\text{netOH+NO}}$ 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.

The calculation of $P_{\text{OH+NO}}^{\text{net}}$ has therefore been corrected using the OH concentration ($2.5 \times 10^5 \text{ cm}^{-3}$ molecule⁻¹). We have modified the sentence in the revised text.

L 293-295: The mean value of $P_{\text{OH+NO}}^{\text{net}}$ was 0.33 ppbv h^{-1} , and the specific values in CD, PD, and SPD periods were 0.13, 0.26, and 0.56 ppbv h^{-1} , respectively.

Finally, the discussion and conclusion of the article on this point were also revised consequently.

L 316-318: ...Second, the hourly rate of HONO abatement pathways, except OH + HONO, should be at least 0.22 ppbv h^{-1} (i.e., $3.36 - 1.59 \text{ ppbv}$)/8 h)...

L 549-550: The mean value of $P_{\text{OH+NO}}^{\text{net}}$ in the CD, PD, and SPD periods were 0.13, 0.26, and 0.56 ppbv h⁻¹, respectively.

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.

Response: Sorry for my confusion. The equations 4 to 6 have been moved before all the paragraphs. We have modified the sentences in the revised text.

L 454-465: The expression of $d \text{ HONO} / d t$ represents the observed variations of hourly HONO concentrations, for which we can use $\Delta \text{ HONO} / \Delta d t$ instead:

$$\begin{aligned} d \text{ HONO} / d t &= \text{sources} - \text{sinks} \\ &= (P_{\text{unknown}} + P_{\text{OH+NO}} + P_{\text{emi}} + P_{\text{het}}) - (L_{\text{OH+HONO}} + L_{\text{photo}}) \end{aligned} \quad (4),$$

$$P_{\text{OH+NO}} = k_{\text{OH+NO}} [\text{OH}] [\text{NO}] \quad (5),$$

$$L_{\text{OH+HONO}} = k_{\text{OH+HONO}} [\text{OH}] [\text{HONO}] \quad (6).$$

The $d \text{ HONO} / d t$ calculated from the measurements was small and evenly distributed around zero (Li et al., 2012). P_{unknown} is the production rate by an unknown daytime HONO source. $P_{\text{OH+NO}}$ is the rate of reaction of NO and OH. P_{emi} represents the direct emission rate of HONO from combustion processes. By studying the source and reduction, the daytime HONO budget was analyzed with Eq. (4) (Su et al., 2008).

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 $d \text{ HONO} / d t$ 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.

Response: Sorry for my careless. P_{unknown} is calculated by:

$$d \text{ HONO} / d t = (P_{\text{unknown}} + P_{\text{OH+NO}} + P_{\text{emi}} + P_{\text{het}}) - (L_{\text{OH+HONO}} + L_{\text{photo}});$$

$$P_{\text{unknown}} = L_{\text{OH+HONO}} + L_{\text{photo}} - P_{\text{OH+NO}} - P_{\text{emi}} - P_{\text{het}}.$$

The sentence has been added in the revised text.

L 460-461: The $d \text{ HONO} / d t$ calculated from the measurements was small and evenly distributed around zero (Li et al., 2012).

We have studied the correlation between the unknown source of HONO and the $\text{PM}_{2.5}$ mass concentrations was lower. So, we can not probably use the P_{unknown} calculated to perform this correlation for explaining the unknown source. The unknown sources of HONO may include the NO_2 photolysis of sooty surface and adsorbed nitric acid and nitrate at UV wavelengths (Kleffmann et al., 1999). The homogeneous nucleation of NO_2 , H_2O , and NH_3 is the HONO formation pathway (Zhang and Tao, 2010). In the meanwhile, HONO can deposit and react with amines in forming nitrosamines (Li et al., 2012) for sinking.

This further analysis and method are not found yet.

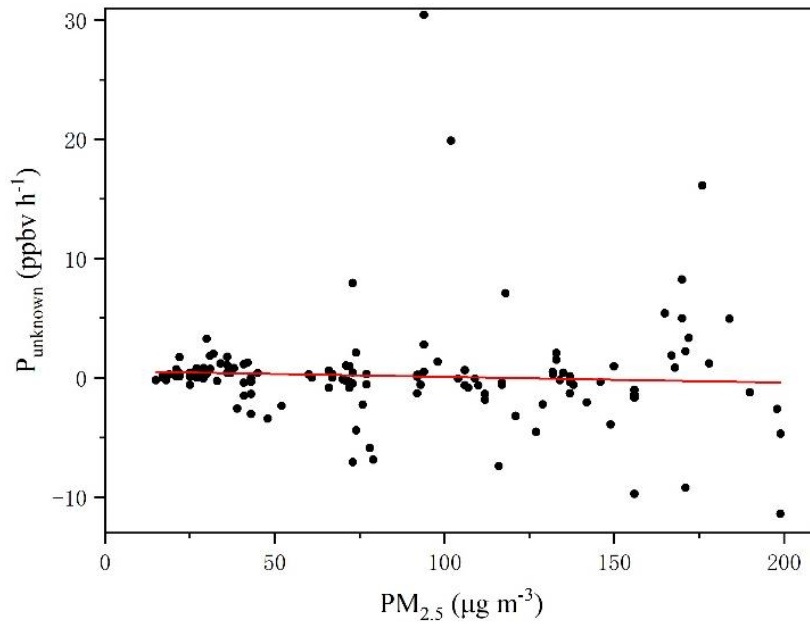


Figure The correlation between $PM_{2.5}$ and P_{unknown} .

Minor comments:

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

Response: OK. We have added the word, “When”, in the revised text.

L 21-23: ...under high- NO_x conditions (i.e., when the concentration of NO was higher than...

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

Response: Thank you. We have removed the word, “abatement”, in the revised text.

L 32-33: The hourly level of HONO abatement pathways, except for...

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

Response: OK. We have removed the word, “also”, in the revised text.

L 48-49: ·OH is an important oxidant in the atmosphere, and it can react with organic substances...

4. -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.

Response: Sorry for the confusion. We explored the sources and characteristics of HONO at different pollution levels, as well as the reaction mechanism. We have not explained the reaction mechanism and pathways, so we have changed “reaction” for “the changes in the contribution of the homogeneous reaction, heterogeneous conversion, and direct emission”. This sentence has been changed in the revised text.

L 51-54: Therefore, the changes in the contribution of the homogeneous reaction, heterogeneous conversion, and direct emission during pollution can be observed by studying the formation mechanism of HONO.

5. -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”.

Response: Thank you for your comment. We have changed “Nitro-Mac” for “wet chemical derivatization technique-HPLC/UV-VIS detection”. We have modified the sentence in the revised text.

L 58-69: ...wet chemical derivatization technique-HPLC/UV-VIS detection...

6. -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.

Response: Sorry for my carelessness. We have analyzed and explored these techniques, and the important techniques have been added in the same sentence in the revised text.

L 55-62: Several instruments have been used to determine ambient HONO concentrations, and these include differential optical absorption spectrophotometer (DOAS) (Elshorbany et al., 2012; Winer and Biermann, 1994), long path absorption photometer (LOPAP) (Heland et al., 2001), wet chemical derivatization technique-HPLC/UV-VIS detection (Michoud et al., 2014), stripping coil-UV/Vis absorption photometer (SC-AP) (Pinto et al., 2014), IBBCEAS (Duan et al., 2018; Min et al., 2016), CIMS (Hirokawa et al., 2009; Roberts et al., 2010), and ambient ion monitor (AIM) (VandenBoer et al., 2014).

7. -P3, line 72: Change “be absorbed by” for “react with”.

Response: OK. We have modified the sentence in the revised text.

L 76-77: ...HONO can react with the ·OH...

8. -P5, lines 137-138: “The site is close to the West Fourth Ring Road”. How far is it? Please be more precise.

Response: Sorry for my carelessness. We will be more precise in the full text and

examine the logic problems. The sentence has been changed in the revised text.

L 160-162: The site is about 500 m from the western Fourth-Ring Expressway of Zhengzhou City and about 2 km from Lian Huo Expressway to the north.

9. -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.

Response: OK , we have changed “High-Time-resolution instrument” for “Instruments”. And, the title has been modified, “Characteristics, sources, and reactions of nitrous acid during winter at an urban site in the Central Plains Economic Region in China”, in the revised text.

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

Response: Sorry for my carelessness. The sentence has been modified in the revised text.

L 74: ...several gases (e.g., O₂ and N₂) were expelled...

11. -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?

How is it compatible with the frequency of replacement given here and the frequency of calibration? Please clarify.

Response: OK. This is my omission. During the measurement, we have replaced the filter once a week and ensured enough hydrogen peroxide for absorbing

HONO by the denuder. The instrument parts and consumables should be changed before the observation process, and the sampling flow should be calibrated to reduce the negative effect of accessories. The sentence has been modified in the revised text.

L 189-191: The instrument parts and consumables should be changed before the observation process, and the sampling flow should be calibrated to reduce the negative effect of accessories.

And we have added the sentence in the revised text.

L 185-187: Before this measurement period, the membrane of the denuder has been replaced and standard anion and cation solutions have been prepared on Jan. 3rd.

The standard curve has been drawn to ensure the appropriateness of the correlation coefficient (≥ 0.999) and the accuracy of the sample retention time and response value. There is no need to stop the instrument during the replacement of the parts, and the calibration has been completed before the measurement period. The calibration can be used for one to two months at a time.

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

Response: Sorry. We have modified the table heading in the revised text.

Table 1 Data statistics of HONO, PM_{2.5}, NO₂, NO, NO_x, HONO/NO₂, HONO/NO_x, O₃, CO, T, RH, and WS during the measurement period, mean value \pm standard deviation.

13. -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.

Response: OK. We have put the diurnal variation of HONO during the entire period in **Fig. 3** and analyzed the diurnal variation of HONO in the three periods in **Fig. 4(a)** in the revised text. And, we have modified the sentence in the revised text.

L 232-234: The diurnal variations of HONO during the measurement were similar in the three periods, as shown in **Fig. 3** and **Fig. 4**.

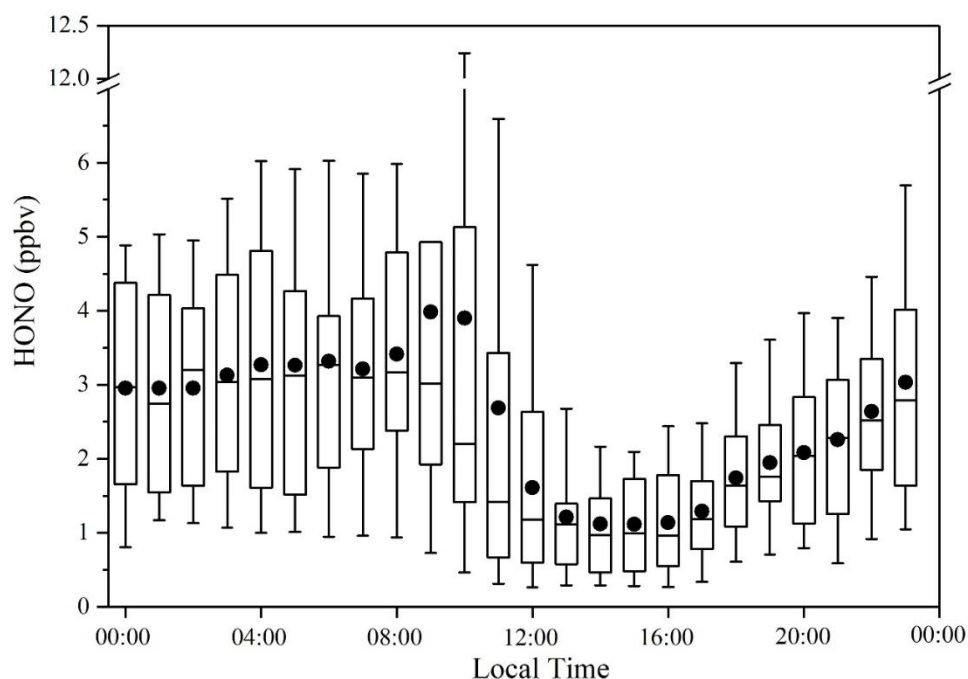


Fig. 3. Diurnal variations of HONO during the measurement.

14. -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.

Response: Thank you for your comment. The sentence has been modified in the revised text.

L 242-243: The NO concentration decreased rapidly in the forenoon, and remained low in the afternoon.

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

Response: OK. We have modified the sentence in the revised text.

L 275-276: [OH] is the concentration of ·OH that was not measured during the campaign.

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

Response: Sorry for my carelessness. The units have been modified in the full text.

L 282: ...2.5×10⁵ molecule cm⁻³.

L 286:...3 to 6×10⁵ molecule cm⁻³...

L 493-498: The mean values of J_{HONO} and ·OH concentration in the CD, PD, and SPD periods were 5.93×10⁻⁴, 3.79×10⁻⁴, and 3.79×10⁻⁴ molecule cm⁻³ and 4.10×10⁶, 2.93×10⁶, and 3.76×10⁶ molecule cm⁻³, respectively. The results of the calculated OH radicals ranged from (0.58–11.49) ×10⁶ molecule cm⁻³, and the mean value was 3.57 ×10⁶ molecule cm⁻³ at noon in Zhengzhou.

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

Response: Thank you. We have removed the word, “abatement”, in the revised

text.

L 316-317: Second, the hourly level of HONO abatement pathways, except OH + HONO, should be at least 0.22 ppbv h^{-1} (i.e., $3.36 - 1.59 \text{ ppbv}$)/8 h).

18. -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., $13.41 - 1.59 \text{ ppbv}$) / 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 $P_{\text{netOH+NO}}$ 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.

Response: Thank you for your comment. At night, in addition to reaction with HONO to OH, there were two HONO removal pathways: heterogeneous loss on aerosols and deposition (Li et al., 2012). The heterogeneous loss of aerosols can not be calculated directly. And, the main factor of the dry deposition on ground surfaces is the deposition velocity of HONO. The reported value of deposition velocity ranged from 0.092 to 2 cm s^{-1} (Harrison et al., 1996; Stutz, 2002). Sorry, we can not give a raw estimation of loss by deposition, but what we can be sure of is that the phenomenon may arise because the dry deposition on ground surfaces can be the main HONO removal pathway at night.

So this is my confusion. This statement is maintained after the recalculation of $P_{\text{OH+NO}}^{\text{net}}$ using a more realistic nocturnal OH concentrations, the dry deposition on ground surfaces can be the HONO removal pathway at night. We have changed “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).” for “This phenomenon may arise because the dry deposition on ground surfaces can be the main HONO removal pathway at night, similar to a previous study (Li et al., 2012).” in the revised text (L 318-320).

19. -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 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.

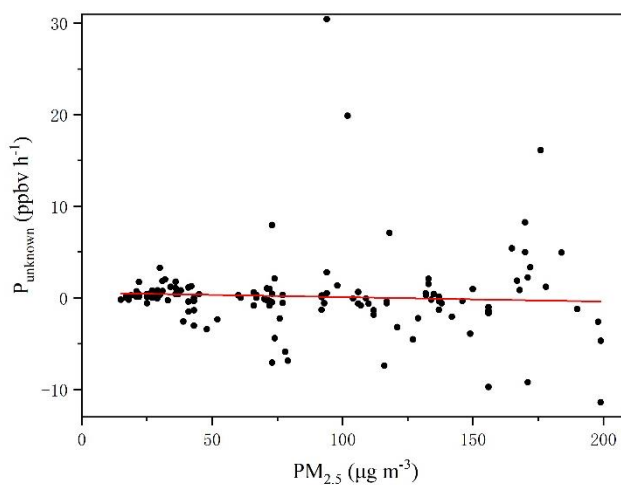
Response: Thank you. This is my carelessness. The fair correlation between HONO concentrations and PM_{2.5} mass concentrations did not explain the importance of HONO heterogeneous formation pathways on aerosol surfaces. What we want to explain is whether there is a change in the intensity of NO₂ heterogeneous reactions during the increase in heavy pollution levels, so we found a relevant explanation (Cui et al., 2018). Cui et al. (2018) studied the more intense heterogeneous conversion of NO₂ to HONO on particle surfaces during the pollution episodes at a single particle scale. We have modified the sentences in the revised text.

L 382-386: The fair correlation between HONO and PM_{2.5} may pinpoint the mainly anthropogenic origins of these two pollutants with the high direct or indirect contribution of combustion sources. The reason for the increased HONO during the heavy pollution period could be by the comparatively high loading and large particle surface (Cui et al., 2018).

A correlation between the calculated unknown source of HONO and the 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.

We have studied the correlation between the unknown source of HONO and the $\text{PM}_{2.5}$ mass concentrations was lower. So, we can not probably use the P_{unknown} calculated in section 3.3 to perform this correlation for explaining the unknown source.



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

Response: Sorry for my carelessness. The sentence has been modified in the revised text.

L 432: ...HONO was calculated in the current study...

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

Response: OK. The sentence has been modified in the revised text.

L 442-443: The averaged conversion rates...

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

Response: OK. The sentence has been modified in the revised text.

L 445: The increase in the conversion rate...

23. -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.

Response: Sorry for my confusion. The exact uptake coefficients of NO₂ on ground and aerosol surfaces are variable and should be different (Harrison and Collins, 1998). The present analysis simplified this process by treating the ground and aerosol surfaces the same. The uptake coefficient is mainly dependent on the surface characteristics, e.g. surface area, surface type (Lu et al., 2018). We have added the sentences in the revised text.

L 448-452: The exact uptake coefficients of NO₂ on ground and aerosol surfaces are variable and should be different (Harrison and Collins, 1998). The present analysis simplified this process by treating the ground and aerosol surfaces the same. The uptake coefficient is mainly dependent on the surface characteristics, e.g. surface type and moisture (Lu et al., 2018).

24. -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 O₃ 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.

Response: OK. Sorry for my carelessness. The problem you pointed out is correct. TUV is an interactive model for calculation of photodissociation coefficients (J values) over the visible and ultraviolet spectral range in the atmosphere under clear sky conditions. The J_{HONO} values obtained this way were assumed in clear sky days without clouds. We would add a description of O_3 column and the surface albedo. O_3 column density measured by the Ozone Monitoring Instrument (OMI, data available at <https://ozonewatch.gsfc.nasa.gov/data/omi/Y2019/>). The O_3 column density ranges from 292 to 306 DU during the entire period. The experimental site being situated in an urban region, the surface albedo is considered as 0.13 (Sailor, 1995). The ground elevation and the measurement altitude are 168 and 188 m respectively.

So we have added the sentences in the revised text.

L 478-484: The J_{HONO} values obtained this way were assumed in clear sky days without clouds. O_3 column and the surface albedo. O_3 column density measured by the Ozone Monitoring Instrument (OMI, data available at <https://ozonewatch.gsfc.nasa.gov/data/omi/Y2019/>). The O_3 column density ranges from 292 to 306 DU during the entire period. The experimental site being situated in an urban region, the surface albedo is considered as 0.13 (Sailor, 1995). The ground elevation and the measurement altitude are 168 and 188 m respectively.

25. -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.

Response: Thank you for your comment. This part of the formulas of NO_2 , O_3 , and JO^1D has been described a lot in the paper (Rohrer and Berresheim, 2006). Sorry

for my carelessness. We have placed this part in the revised supplement.

2. The concentration of OH radicals was calculated with the formulas of NO₂, O₃, and J_{O¹D}.

$$[\text{OH}] = \frac{k_{\text{HO}_2+\text{NO}}\tau_{\text{HC}}[\text{NO}_2]F_{\text{J}}}{k_{\text{NO}+\text{O}_3}} \times \sqrt{\frac{\alpha}{k_{\text{HO}_2+\text{HO}_2}[\text{O}_3]}} \times J(O^1D),$$

where [OH] represents the concentration of OH radicals, $k_{\text{HO}_2+\text{NO}} = 8.56 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $\tau_{\text{HC}} = 0.3 \text{ s}$, [NO₂] represents the NO₂ concentration, $F_{\text{J}} = 2 \text{ s}^{-0.5}$, $k_{\text{NO}+\text{O}_3} = 1.82 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $\alpha = 0.075$, $k_{\text{HO}_2+\text{HO}_2} = 8.56 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, [O₃] represents the O₃ concentration, and $J(O^1D)$ represents the O^1D efficiency of photolysis.

We have modified the sentence in the revised text.

L 484-485: The concentration of OH radicals was calculated with the formulas of NO₂, O₃, and J_{O¹D} in the supplement.

26. -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.

Response: OK. TUV can only calculate the photolysis efficiency under daylight conditions. So, J_{HONO} and ·OH concentration are the mean values at noon. To prevent this confusion, we have modified the sentence in the revised text.

L 495-500: The mean values of J_{HONO} and ·OH concentration at noon in the CD, PD, and SPD periods were 5.93×10^{-4} , 3.79×10^{-4} , and 3.79×10^{-4} molecule cm⁻³ and 4.10×10^6 , 2.93×10^6 , and 3.76×10^6 molecule cm⁻³, respectively.”

27. -P17, lines 454-455: “Although the values of P_{OH+NO} had high uncertainty because of the NO concentrations”. How NO concentrations can affect largely the uncertainties of P_{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.

Response: Sorry. This sentence is my expression problem. What I mean is that the concentration of NO has a great influence on it, but the homogeneous reaction is still an important pathway. The uncertainty of NO measurements was shown in **Table S1**.

So we have changed “Although the values of $P_{\text{OH}+\text{NO}}$ had high uncertainty because of the NO concentrations, $P_{\text{OH}+\text{NO}}$ contributed the most to HONO production during daytime.” for “The concentration of NO has a great influence on $P_{\text{OH}+\text{NO}}$, so the homogeneous reaction is still an important pathway of HONO production during the daytime.” in the revised text (L 516-518).

28. -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 $J_{\text{O}^1\text{D}}$ 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.

Response: OK. We have modified the problem in **Fig. 9**.

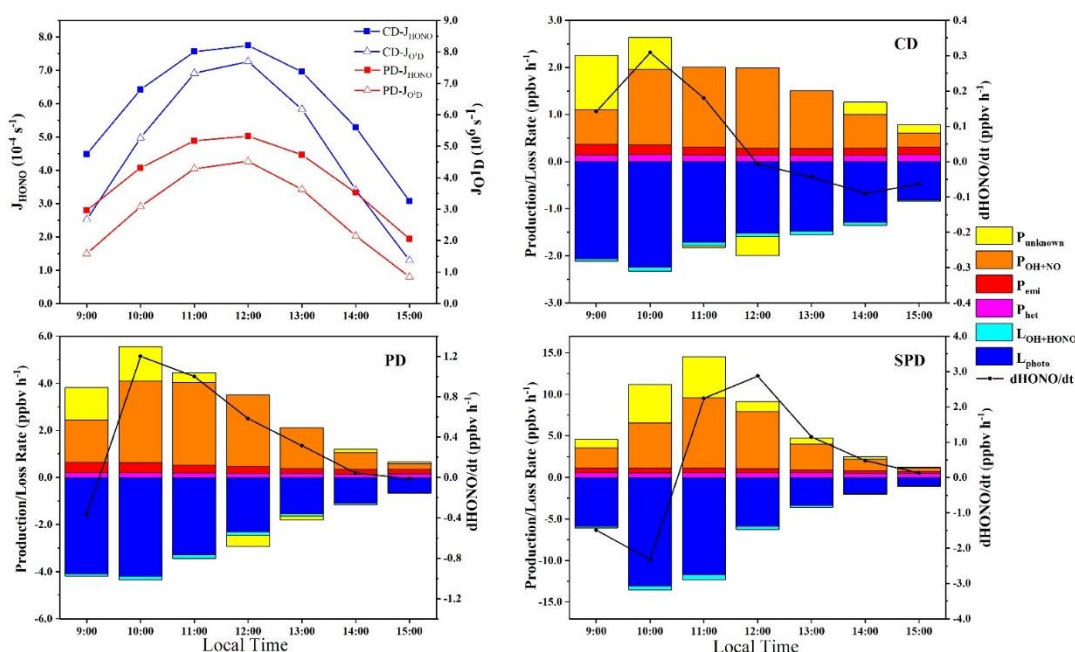


Fig. 9. The average profiles of J_{HONO} and $J_{\text{O}^1\text{D}}$ concentrations during the daytime, and production and loss rate of the daytime HONO in CD, PD and SPD periods.

We treated PD and SPD the same. The reason is that the main input parameters of TUV cannot be obtained directly, so we quoted the input parameters in the literature. However, the input parameters of PD and SPD are not distinguished in the papers. We wanted to study that under the same output conditions from the TUV model, the impact of different pollution levels changed on the daytime budget. We have added the sentence in the revised text.

L 491-493: We wanted to study that under the same output conditions from the TUV model in the PD and SPD periods, the impact of different pollution levels changed on the daytime budget.

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

Response: Sorry. We have removed the word, “WD”, in the revised text.

Table 1. Data statistics of HONO, $\text{PM}_{2.5}$, NO_2 , NO, NO_x , HONO/ NO_2 , HONO/ NO_x , O_3 , CO, T, RH, and WS during the measurement period, mean value \pm standard deviation.

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

Qi Hao, Nan Jiang*, Ruiqin Zhang, Liuming Yang, and Shengli Li

Key Laboratory of Environmental Chemistry and Low Carbon Technologies of Henan Province, Research Institute of Environmental Science, College of Chemistry, School of Ecology and Environment, Zhengzhou University, Zhengzhou 450001, China

Supplement:

1. This AIM method and its details.

HONO was hygroscopically grown in the parallel plate denuder and collected as an aqueous solution in a cyclone assembly. The aqueous sample aliquots from both channels were transported to the ion chromatographic systems housed inside a ground container for hourly semicontinuous online analysis of HONO. The ion chromatographic system was calibrated for NO_2^- using mixed anion standard solutions of NO_2^- .

2. The concentration of OH radicals was calculated with the formulas of NO_2 , O_3 , and $J(O^1D)$.

$$[\text{OH}] = \frac{k_{\text{HO}_2+\text{NO}}\tau_{\text{HC}}[\text{NO}_2]F_J}{k_{\text{NO}+\text{O}_3}} \times \sqrt{\frac{\alpha}{k_{\text{HO}_2+\text{HO}_2}[\text{O}_3]}} \times J(O^1D),$$

where $[\text{OH}]$ represents the concentration of OH radicals, $k_{\text{HO}_2+\text{NO}} = 8.56 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $\tau_{\text{HC}} = 0.3 \text{ s}$, $[\text{NO}_2]$ represents the NO_2 concentration, $F_J = 2 \text{ s}^{-0.5}$, $k_{\text{NO}+\text{O}_3} = 1.82 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $\alpha = 0.075$, $k_{\text{HO}_2+\text{HO}_2} = 8.56 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $[\text{O}_3]$ represents the O_3 concentration, and $J(O^1D)$ represents the O^1D efficiency of photolysis.

Figure Captions:

Fig. S1. The correlation study between $\text{HONO}_{\text{correct}}$ and NO_2 in the nighttime.

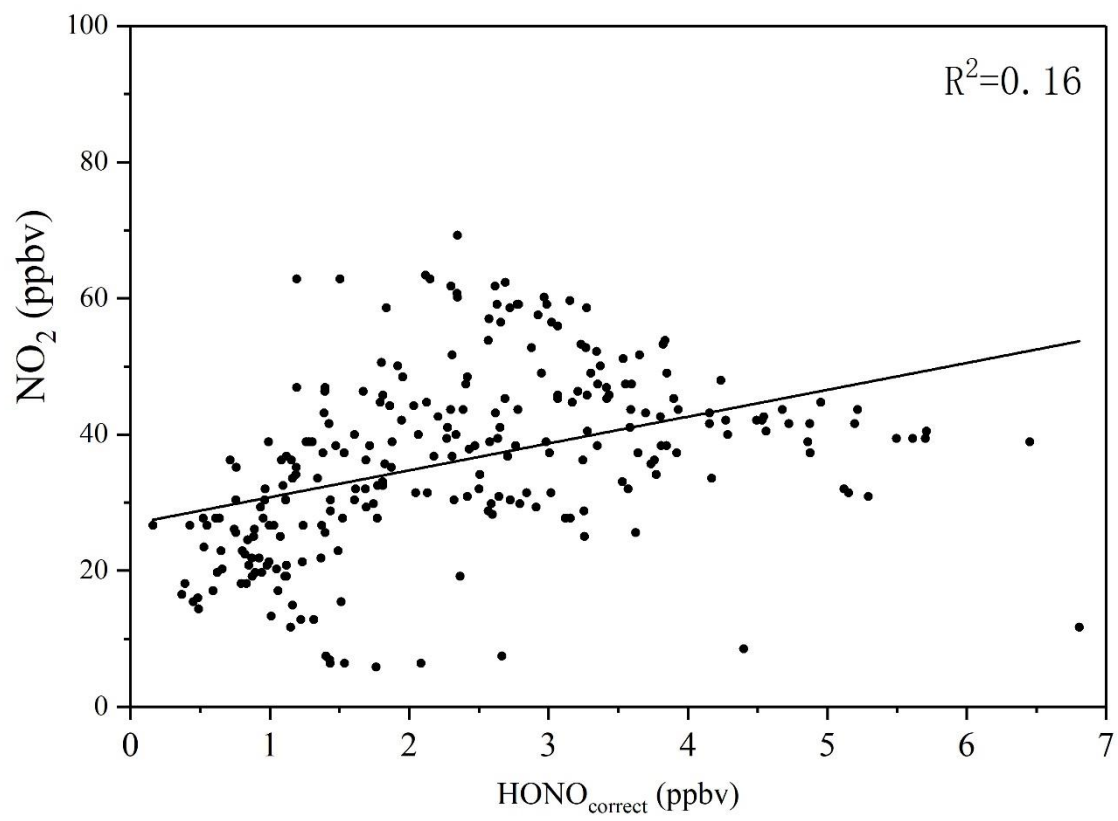


Fig. S1. The correlation study between HONO_{correct} and NO₂ in the nighttime.

Table Captions:

Table S1. Measured species and performance of the instruments.

Table S2 The error bars of Fig. 4. (The units of all species except HONO/NO₂ and HONO/NO_x are ppbv. The units of HONO/NO₂ and HONO/NO_x are %.)

Table S3 The error bars of Fig. 5. (The units of all species except $P_{\text{OH+NO}}^{\text{net}}$ are ppbv. The unit of $P_{\text{OH+NO}}^{\text{net}}$ is ppbv/h.)

Table S4 The error bars of Fig. 8. (The units of all species except HONO_{correct}/NO₂ are ppbv. The unit of HONO_{correct}/NO₂ is %.)

Table S1. Measured species and performance of the instruments.

Species	Measurement technique	Detection limit	Accuracy
PM _{2.5}	Tapered Element Oscillating Microbalance	1.5 $\mu\text{g m}^{-3}$	$\pm 5\%$
HONO	Ion Chromatography	4 pptv	$\pm 20\%$
CO	Absorbs Infrared Radiation	40 ppbv	$\pm 5\%$
NO	Chemiluminescence	60 pptv	$\pm 20\%$
NO ₂	Chemiluminescence	300 pptv	$\pm 20\%$
O ₃	UV Photometry	0.5 ppbv	$\pm 5\%$

The results came from instrument manufacturers.

Table S2-1 The error bars of Fig. 4. (The units of all species except HONO/NO₂ and HONO/NO_x are ppbv. The units of HONO/NO₂ and HONO/NO_x are %.)

Species-period	Local Time (hh:mm)									
	00:00	01:00	02:00	03:00	04:00	05:00	06:00	07:00	08:00	09:00
HONO-CD	1.7 ± 1.3	1.4 ± 0.6	1.3 ± 0.4	1.2 ± 0.3	1.2 ± 0.2	1.2 ± 0.2	1.4 ± 0.3	1.5 ± 0.6	1.7 ± 0.9	1.6 ± 0.9
HONO-PD	3.2 ± 1.5	3.1 ± 1.3	3 ± 1.1	3.3 ± 1.2	3.5 ± 1.3	3.5 ± 1.2	3.6 ± 1.1	3.3 ± 0.9	3.7 ± 1.6	4.1 ± 2.8
HONO-SPD	3.7 ± 0.9	4 ± 0.8	4.2 ± 0.6	4.4 ± 0.8	4.6 ± 1	4.6 ± 1.2	4.6 ± 1.5	4.4 ± 1.3	4.4 ± 1.1	5.7 ± 3
NO-CD	14.3 ± 17	9 ± 9.7	8.5 ± 12.7	10.1 ± 22.4	10.6 ± 21.1	21.9 ± 29	27.8 ± 33	40.1 ± 51	52.6 ± 79	55.5 ± 84
NO-PD	57.3 ± 48	62.7 ± 55.9	49.6 ± 49	44 ± 47.8	47 ± 48.7	46.6 ± 30	41.4 ± 34	44.7 ± 33	48.9 ± 35	53.7 ± 44
NO-SPD	79.4 ± 103	100.1 ± 118	128.3 ± 133	129 ± 134	111 ± 119	117 ± 95	100 ± 94	88.4 ± 85	82.3 ± 70	85.4 ± 71
NO ₂ -CD	25.4 ± 8.2	25.6 ± 9.9	24.7 ± 10.5	22.9 ± 10.4	24 ± 11.4	20.7 ± 11	20.2 ± 9	23.6 ± 11	28.6 ± 18	28.6 ± 18
NO ₂ -PD	41.1 ± 10	40.8 ± 11.2	39.7 ± 10.7	37.9 ± 7.1	36.6 ± 5.4	35.9 ± 5	33.8 ± 6	34.4 ± 6	33.2 ± 5	30.7 ± 6
NO ₂ -SPD	45.3 ± 9.5	43.5 ± 9.2	42.8 ± 8.8	42.1 ± 8.2	42.2 ± 8.1	41 ± 7.1	40.6 ± 6.9	40.7 ± 6	40.1 ± 6	39.2 ± 7
O ₃ -CD	14.2 ± 10	13.6 ± 10.4	14.2 ± 10.1	14.9 ± 9.4	13.6 ± 9.1	11.7 ± 10	13.8 ± 10	12.9 ± 9	11.6 ± 8	12.1 ± 7
O ₃ -PD	6.6 ± 6.1	6.4 ± 5.2	7.1 ± 5.2	6.3 ± 3.3	4.7 ± 2.2	5.3 ± 3	7.7 ± 6.9	5.3 ± 2.8	5.5 ± 3	7.1 ± 4
O ₃ -SPD	7.8 ± 6.4	7.7 ± 6.2	7.3 ± 5	6 ± 2.9	5.3 ± 2.3	5 ± 2.1	5.6 ± 2.5	5.2 ± 2.2	5.6 ± 2.6	6 ± 2.6
HONO/NO ₂ -CD	3.8 ± 1.5	4.4 ± 1	4.4 ± 1.1	4.9 ± 1	5.1 ± 0.8	8.3 ± 6	6.9 ± 2.1	6.2 ± 1.4	5.1 ± 0.8	4.3 ± 1.1
HONO/NO ₂ -PD	8 ± 3.6	7.8 ± 3.4	8 ± 3.3	9 ± 3.7	10 ± 4.5	10.1 ± 4	11.2 ± 4.6	10.3 ± 4	12.1 ± 7	14.3 ± 11
HONO/NO ₂ -SPD	8.3 ± 1.9	9.3 ± 1.4	10 ± 1.5	10.7 ± 1.9	11 ± 2.2	11.3 ± 3	11.5 ± 3.9	10.9 ± 3	11.1 ± 2	15 ± 8.3
HONO/NO _x -CD	2.7 ± 1.4	3.7 ± 1.5	4.2 ± 1.4	4.9 ± 1.1	4.9 ± 1	5.3 ± 2.5	5.1 ± 2.9	4.5 ± 2.4	3.6 ± 1.5	2.8 ± 1.4
HONO/NO _x -PD	4.4 ± 1.4	4.3 ± 1.7	4.6 ± 1.5	5.3 ± 1.3	5.3 ± 1	5.3 ± 1.1	6.6 ± 2.7	5.9 ± 2.3	6.5 ± 3.8	6.6 ± 4.3
HONO/NO _x -SPD	5.1 ± 2	5.3 ± 2.4	5.4 ± 3.4	5.8 ± 3.9	6.1 ± 3.9	5.7 ± 3.7	5.9 ± 3.6	5.7 ± 3	5.8 ± 2.9	6.7 ± 3.1

Table S2-2 The error bars of Fig. 4. (The units of all species except HONO/NO₂ and HONO/NO_x are ppbv. The units of HONO/NO₂ and HONO/NO_x are %.)

Species-period	Local Time (hh:mm)									
	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	19:00
HONO-CD	1.1 ± 0.6	0.6 ± 0.3	0.5 ± 0.3	0.6 ± 0.4	0.6 ± 0.5	0.7 ± 0.5	0.6 ± 0.5	0.7 ± 0.4	1 ± 0.5	1.2 ± 0.5
HONO-PD	2.9 ± 1.9	1.9 ± 1.3	1.3 ± 0.7	1 ± 0.3	0.9 ± 0.3	0.9 ± 0.3	0.9 ± 0.3	1.1 ± 0.4	1.4 ± 0.3	1.7 ± 0.3
HONO-SPD	6.9 ± 4.3	5.2 ± 3.8	3 ± 1.3	2.1 ± 0.7	1.8 ± 0.7	1.7 ± 0.6	1.8 ± 0.7	2 ± 0.5	2.7 ± 0.7	2.8 ± 0.8
NO-CD	43.9 ± 69.8	27.9 ± 40.8	14.9 ± 17.1	10.3 ± 7.8	7.3 ± 3	6 ± 4.5	6.4 ± 5.6	3.6 ± 3.4	2.6 ± 3.2	5.9 ± 7.7
NO-PD	49.3 ± 45.2	30 ± 26.2	21 ± 20.7	12.7 ± 14.7	9.4 ± 12.3	8.4 ± 9.5	5.7 ± 4.7	6.3 ± 6.8	9 ± 9	10 ± 10.3
NO-SPD	90.8 ± 73.4	79.3 ± 69.3	57.1 ± 52.3	34.8 ± 36.4	24.5 ± 28.7	19 ± 24.7	15 ± 18.8	11.8 ± 11	11.8 ± 7.9	22.4 ± 21
NO ₂ -CD	26.8 ± 15.7	22.7 ± 9.2	17.6 ± 7.1	17.1 ± 9	19.6 ± 9.6	21 ± 10.7	20.5 ± 9	21.4 ± 9	26 ± 12.5	30 ± 13.7
NO ₂ -PD	30 ± 6.9	28.8 ± 7.7	27.4 ± 9.6	24.8 ± 9.4	22.5 ± 10.6	25 ± 9.9	25.7 ± 9.3	27.1 ± 9	35 ± 8.7	36.2 ± 9.2
NO ₂ -SPD	39.8 ± 7.8	41.5 ± 8.3	42.3 ± 10.1	39.5 ± 12.6	38.5 ± 14.3	38 ± 14.7	38 ± 13.9	42 ± 15.4	45 ± 11.5	47 ± 10.8
O ₃ -CD	15.9 ± 8.8	19.5 ± 9.7	22.6 ± 8.3	25.5 ± 8.5	28.1 ± 9.1	29 ± 10.8	28 ± 10.8	29 ± 10.2	23.6 ± 10	17 ± 8.9
O ₃ -PD	9.6 ± 6.1	12.8 ± 6.2	18.7 ± 8.3	24.1 ± 8.4	28.2 ± 9.7	27 ± 10.8	28 ± 10.4	26 ± 10.5	17.4 ± 8.6	15 ± 11.6
O ₃ -SPD	6.3 ± 2.4	8.7 ± 4.5	12.8 ± 8.5	19.4 ± 12.9	24.1 ± 14.7	28 ± 16.6	29 ± 17.6	25 ± 16.1	17 ± 11.1	10.6 ± 9.7
HONO/NO ₂ -CD	4.1 ± 2.3	3.1 ± 1.9	3.3 ± 1.9	3.3 ± 1.3	3.1 ± 1.3	3.1 ± 1.3	2.9 ± 1.4	3.1 ± 1.4	3.9 ± 1.4	4.5 ± 2.2
HONO/NO ₂ -PD	9.4 ± 5.6	6.2 ± 3	4.7 ± 1.5	4.2 ± 1.2	4.7 ± 2.2	3.9 ± 0.7	3.7 ± 0.4	4.1 ± 1.2	4.3 ± 0.9	5 ± 1.5
HONO/NO ₂ -SPD	18.9 ± 13.7	13.7 ± 12	7.3 ± 3.5	5.6 ± 2.6	4.9 ± 2.1	4.8 ± 2.4	4.9 ± 1.6	5 ± 1	6.3 ± 1.8	6.2 ± 1.5
HONO/NO _x -CD	2.9 ± 2.1	2.2 ± 1.5	2.4 ± 1.5	2.5 ± 1.1	2.5 ± 1	2.6 ± 0.9	2.5 ± 0.9	2.8 ± 1	3.7 ± 1.1	4.1 ± 1.9
HONO/NO _x -PD	4.8 ± 2.4	3.8 ± 1.3	3.5 ± 1.2	3.5 ± 1.5	4 ± 2.1	3.4 ± 0.9	3.3 ± 0.5	3.7 ± 1.2	3.8 ± 0.7	4.3 ± 1.5
HONO/NO _x -SPD	8.2 ± 5.8	6.9 ± 5.7	4.3 ± 2	4 ± 2	3.8 ± 1.6	3.9 ± 1.9	4.3 ± 1.6	4.5 ± 1.2	5.5 ± 1.5	4.9 ± 1.3

Table S2-3 The error bars of Fig. 4. (The units of all species except HONO/NO₂ and HONO/NO_x are ppbv. The units of HONO/NO₂ and HONO/NO_x are %.)

Species-period	Local Time (hh:mm)			
	20:00	21:00	22:00	23:00
HONO-CD	1.3 ± 0.6	1.6 ± 0.9	2 ± 0.9	2.1 ± 0.9
HONO-PD	1.7 ± 0.7	1.8 ± 0.8	2 ± 0.9	2.1 ± 0.9
HONO-SPD	3.1 ± 0.9	3.2 ± 0.9	3.7 ± 0.8	4.6 ± 1.2
NO-CD	11.1 ± 16.9	14.5 ± 22.5	35.5 ± 68.9	50.8 ± 99.2
NO-PD	15 ± 14.1	15.3 ± 14.7	27.4 ± 28.5	33.9 ± 28.9
NO-SPD	29.4 ± 24.2	37.3 ± 26.6	38.5 ± 23.1	51.4 ± 31.4
NO ₂ -CD	31 ± 13.8	30.3 ± 14.5	31.6 ± 13.6	31 ± 14.3
NO ₂ -PD	37.3 ± 10.5	38.5 ± 13.9	38.3 ± 13.5	37.1 ± 13.2
NO ₂ -SPD	44.5 ± 11	43.5 ± 11.5	43.5 ± 11.1	42.1 ± 13.1
O ₃ -CD	13.3 ± 10.1	14 ± 11	12.2 ± 8.7	12.7 ± 8.8
O ₃ -PD	13.7 ± 10.3	10.9 ± 8.5	10.9 ± 7.7	12.2 ± 10.4
O ₃ -SPD	9.9 ± 8.6	10.8 ± 9.2	9.7 ± 8.7	9.6 ± 9.6
HONO/NO ₂ -CD	4.6 ± 2.2	5.7 ± 2.6	6.5 ± 2.6	6.8 ± 2.7
HONO/NO ₂ -PD	4.7 ± 1.9	4.6 ± 1.2	4.9 ± 0.8	5.3 ± 0.8
HONO/NO ₂ -SPD	7 ± 1.5	7.5 ± 1.4	8.9 ± 2.3	9.4 ± 2.4
HONO/NO _x -CD	4 ± 1.9	4.8 ± 2.2	4.9 ± 2.8	5 ± 3
HONO/NO _x -PD	3.9 ± 2.1	3.9 ± 1.3	3.8 ± 1	3.8 ± 0.9
HONO/NO _x -SPD	5.1 ± 1.5	5.2 ± 2	5.8 ± 2	5 ± 1.4

Table S3-1 The error bars of Fig. 5. (The units of all species except P_{OH+NO}^{net} are ppbv. The unit of P_{OH+NO}^{net} is ppbv/h.)

Species-period	Local Time (hh:mm)									
	19:00	20:00	21:00	22:00	23:00	00:00	01:00	02:00	03:00	04:00
P_{OH+NO}^{net} -CD	0.04 ± 0.06	0.08 ± 0.12	0.11 ± 0.17	0.33 ± 0.54	0.47 ± 0.79	0.12 ± 0.13	0.07 ± 0.08	0.03 ± 0.03	0.01 ± 0.1	0.02 ± 0.1
HONO-CD	1.18 ± 0.48	1.32 ± 0.62	1.62 ± 0.9	2.02 ± 0.94	2.09 ± 0.9	1.67 ± 1.34	1.43 ± 0.63	1.26 ± 0.44	1.2 ± 0.3	1.2 ± 0.22
NO-CD	5.4 ± 6.5	10.2 ± 14.4	13.3 ± 19.2	38.2 ± 62.2	54.9 ± 89.7	15 ± 14.8	8.8 ± 8.6	3.7 ± 4.2	1.5 ± 2.3	2.5 ± 2.6
P_{OH+NO}^{net} -HD	0.07 ± 0.07	0.1 ± 0.1	0.1 ± 0.1	0.19 ± 0.2	0.23 ± 0.2	0.4 ± 0.34	0.44 ± 0.4	0.34 ± 0.35	0.3 ± 0.34	0.3 ± 0.34
HONO-HD	1.7 ± 0.27	1.71 ± 0.68	1.82 ± 0.78	1.98 ± 0.89	2.06 ± 0.93	3.21 ± 1.54	3.05 ± 1.27	3.01 ± 1.08	3.3 ± 1.17	3.5 ± 1.34
NO-HD	8.5 ± 8.4	12.2 ± 11.5	12.5 ± 12	22.4 ± 23.3	27.7 ± 23.6	46.8 ± 39.5	51.2 ± 45.6	40.5 ± 40	35.9 ± 39	38 ± 39.7
P_{OH+NO}^{net} -SHD	0.15 ± 0.15	0.2 ± 0.17	0.25 ± 0.18	0.26 ± 0.16	0.35 ± 0.23	0.55 ± 0.75	0.7 ± 0.85	0.9 ± 0.96	0.9 ± 1.0	0.8 ± 0.86
HONO-SHD	2.8 ± 0.8	3.1 ± 0.9	3.2 ± 0.9	3.7 ± 0.8	4.6 ± 1.2	3.7 ± 0.9	4 ± 0.8	4.2 ± 0.6	4.4 ± 0.8	4.6 ± 1
NO-SHD	18 ± 17	24 ± 20	30 ± 21	31 ± 19	42 ± 25	64 ± 84	81 ± 96	104 ± 108	105 ± 110	90 ± 97

Table S3-2 The error bars of Fig. 5. (The units of all species except $P_{\text{OH+NO}}^{\text{net}}$ are ppbv. The unit of $P_{\text{OH+NO}}^{\text{net}}$ is ppbv/h.)

Species-period	Local Time (hh:mm)	
	05:00	06:00
$P_{\text{OH+NO}}^{\text{net}}$ -CD	0.12 ± 0.18	0.17 ± 0.22
HONO-CD	1.25 ± 0.21	1.36 ± 0.35
NO-CD	13.7 ± 20.9	19.5 ± 25.1
$P_{\text{OH+NO}}^{\text{net}}$ -HD	0.32 ± 0.22	0.28 ± 0.25
HONO-HD	3.5 ± 1.16	3.56 ± 1.09
NO-HD	38 ± 25.2	33.8 ± 28.5
$P_{\text{OH+NO}}^{\text{net}}$ -SHD	0.82 ± 0.87	0.7 ± 0.68
HONO-SHD	4.6 ± 1.2	4.6 ± 1.5
NO-SHD	95.6 ± 99	81.8 ± 77.1

Table S4-1 The error bars of Fig. 8. (The units of all species except HONO_{correct}/NO₂ are ppbv. The unit of HONO_{correct}/NO₂ is %.)

Species-period	Local Time (hh:mm)									
	19:00	20:00	21:00	22:00	23:00	00:00	01:00	02:00	03:00	04:00
HONO _{correct} -CD	1.0 ± 0.4	1.1 ± 0.6	1.4 ± 0.8	1.6 ± 0.7	1.6 ± 0.6	1.4 ± 1.4	1.2 ± 0.7	1.1 ± 0.5	1.1 ± 0.4	1.1 ± 0.2
NO ₂ -CD	30 ± 15	31 ± 15	30 ± 15	34 ± 15	34 ± 15	25 ± 9	24 ± 8	22 ± 8	20 ± 8	20 ± 8
HONO _{correct} /NO ₂ -CD	3.7 ± 2.2	3.9 ± 2.2	4.9 ± 2.6	5.5 ± 2.7	5.7 ± 2.9	11 ± 18.2	8.9 ± 12	8.6 ± 10.8	8.5 ± 9.7	7.7 ± 7.4
HONO _{correct} -HD	1.4 ± 0.3	1.4 ± 0.7	1.5 ± 0.7	1.6 ± 0.8	1.7 ± 0.8	2.7 ± 1.3	2.5 ± 1	2.5 ± 0.8	2.9 ± 0.9	3.1 ± 1.1
NO ₂ -HD	36 ± 9	37 ± 10	39 ± 14	38 ± 13	37 ± 13	41 ± 10	41 ± 11	40 ± 11	38 ± 7	37 ± 5
HONO _{correct} /NO ₂ -HD	4.2 ± 1.5	3.8 ± 2	3.8 ± 1.2	4 ± 0.8	4.4 ± 0.7	6.7 ± 3.1	6.5 ± 2.8	6.7 ± 2.8	7.8 ± 3.1	8.7 ± 3.8
HONO _{correct} -SHD	2.4 ± 0.6	2.6 ± 0.7	2.7 ± 0.7	3.2 ± 0.7	4.1 ± 1.3	3.1 ± 0.8	3.3 ± 0.6	3.4 ± 0.7	3.6 ± 1	3.9 ± 1.1
NO ₂ -SHD	47 ± 11	44 ± 11	43 ± 11	44 ± 11	42 ± 13	45 ± 9	43 ± 9	43 ± 9	42 ± 8	42 ± 8
HONO _{correct} /NO ₂ -SHD	5.4 ± 1.4	6.1 ± 1.4	6.5 ± 1.4	7.8 ± 2.2	14.4 ± 16.7	7 ± 1.9	7.8 ± 1.6	8.1 ± 2.2	8.8 ± 2.8	9.3 ± 2.9

Table S4-2 The error bars of Fig. 8. (The units of all species except HONO_{correct}/NO₂ are ppbv. The unit of HONO_{correct}/NO₂ is %.)

Species-period	Local Time (hh:mm)	
	05:00	06:00
HONO _{correct} -CD	1.0 ± 0.4	1.1 ± 0.6
NO ₂ -CD	30 ± 15	31 ± 15
HONO _{correct} /NO ₂ -CD	3.7 ± 2.2	3.9 ± 2.2
HONO _{correct} -HD	1.4 ± 0.3	1.4 ± 0.7
NO ₂ -HD	36 ± 9	37 ± 10
HONO _{correct} /NO ₂ -HD	4.2 ± 1.5	3.8 ± 2
HONO _{correct} -SHD	2.4 ± 0.6	2.6 ± 0.7
NO ₂ -SHD	47 ± 11	44 ± 11
HONO _{correct} /NO ₂ -SHD	5.4 ± 1.4	6.1 ± 1.4

Reference

- Cui, L., Li, R., Zhang, Y., Meng, Y., Fu, H., and Chen, J.: An observational study of nitrous acid (HONO) in Shanghai, China: The aerosol impact on HONO formation during the haze episodes, *Sci. Total Environ.*, 630, 1057-1070, <https://doi.org/10.1016/j.scitotenv.2018.02.063>, 2018.
- Duan, J., Qin, M., Ouyang, B., Fang, W., Li, X., Lu, K., Tang, K., Liang, S., Meng, F., Hu, Z., Xie, P., Liu, W., and Häsler, R.: Development of an incoherent broadband cavity-enhanced absorption spectrometer for in situ measurements of HONO and NO₂, *Atmos. Meas. Tech.*, 11, 4531-4543, <https://doi.org/10.5194/amt-11-4531-2018>, 2018.
- Elshorbany, Y. F., Steil, B., Brühl, C., and Lelieveld, J.: Impact of HONO on global atmospheric chemistry calculated with an empirical parameterization in the EMAC model, *Atmos. Chem. Phys.*, 12, 9977-10000, <https://doi.org/10.5194/acp-12-9977-2012>, 2012.
- Harrison, R. M., Peak, J. D., and Collins, G. M.: Tropospheric cycle of nitrous acid, *J. Geophys. Res.*, 101, 14429-14439, <https://doi.org/10.1029/96jd00341>, 1996.
- Harrison, R. M., and Collins, G. M.: Measurements of Reaction Coefficients of NO₂ and HONO on Aerosol Particles, *J. Atmos. Chem.*, 30, 397-406, <https://doi.org/10.1023/A:1006094304069>, 1998.
- Heland, J., Kleffmann, J., Kurtenbach, R., and Wiesen, P.: A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere, *Environ. Sci. Technol.*, 35, 3207-3212, <https://doi.org/10.1021/es000303t>, 2001.
- Hirokawa, J., Kato, T., and Mafuné, F.: In Situ Measurements of Atmospheric Nitrous Acid by Chemical Ionization Mass Spectrometry Using Chloride Ion Transfer Reactions, *Anal. Chem.*, 81, 8380-8386, <https://doi.org/10.1021/ac901117b>, 2009.
- Kleffmann, J., Becker, K. H., Lackhoff, M., and Wiesen, P.: Heterogeneous conversion of NO₂ on carbonaceous surfaces, *PCCP*, 1, 5443-5450, <https://doi.org/10.1039/a905545b>, 1999.
- Lelieveld, J., Gromov, S., Pozzer, A., and Taraborrelli, D.: Global tropospheric hydroxyl distribution, budget and reactivity, *Atmos. Chem. Phys.*, 16, 12477-12493, <https://doi.org/10.5194/acp-16-12477-2016>, 2016.
- 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, *Atmos. Chem. Phys.*, 12, 1497-1513, <https://doi.org/10.5194/acp-12-1497-2012>, 2012.
- Lu, X., Wang, Y., Li, J., Shen, L., and Fung, J. C. H.: Evidence of heterogeneous HONO formation from aerosols and the regional photochemical impact of this HONO source, *Environ. Res. Lett.*, 13, <https://doi.org/10.1088/1748-9326/aae492>, 2018.
- Markovic, M. Z., VandenBoer, T. C., and Murphy, J. G.: Characterization and optimization of an online system for the simultaneous measurement of atmospheric water-soluble constituents in the gas and particle phases, *J. Environ. Monit.*, 14, 1872-1884, <https://doi.org/10.1039/c2em00004k>, 2012.

-
- 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.
- Min, K. E., Washenfelder, R. A., Dubé, W. P., Langford, A. O., Edwards, P. M., Zarzana, K. J., Stutz, J., Lu, K., Rohrer, F., Zhang, Y., and Brown, S. S.: A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous acid, nitrogen dioxide, and water vapor, *Atmos. Meas. Tech.*, 9, 423-440, <https://doi.org/10.5194/amt-9-423-2016>, 2016.
- Roberts, J. M., Veres, P., Warneke, C., Neuman, J. A., Washenfelder, R. A., Brown, S. S., Baasandorj, M., Burkholder, J. B., Burling, I. R., Johnson, T. J., Yokelson, R. J., and de Gouw, J.: Measurement of HONO, HNCO, and other inorganic acids by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS): application to biomass burning emissions, *Atmos. Meas. Tech.*, 3, 981-990, <https://doi.org/10.5194/amt-3-981-2010>, 2010.
- Rohrer, F., and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, *Nature*, 442, 184-187, <https://doi.org/10.1038/nature04924>, 2006.
- Sailor, D. J.: Simulated Urban Climate Response to Modifications in Surface Albedo and Vegetative Cover, *J. Appl. Meteorol.*, 34, 1694-1704, <https://doi.org/10.1175/1520-0450-34.7.1694>, 1995.
- Spataro, F., Ianniello, A., Esposito, G., Allegrini, I., Zhu, T., and Hu, M.: Occurrence of atmospheric nitrous acid in the urban area of Beijing (China), *Sci. Total Environ.*, 447, 210-224, <https://doi.org/10.1016/j.scitotenv.2012.12.065>, 2013.
- Stutz, J.: Nitrous acid formation in the urban atmosphere: Gradient measurements of NO₂ and HONO over grass in Milan, Italy, *J. Geophys. Res.*, 107, <https://doi.org/10.1029/2001jd000390>, 2002.
- 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, *J. Geophys. Res.*, 113, D14312-14321, <https://doi.org/10.1029/2007jd009060>, 2008.
- Tan, Z., Rohrer, F., Lu, K., Ma, X., Bohn, B., Broch, S., Dong, H., Fuchs, H., Gkatzelis, G. I., Hofzumahaus, A., Holland, F., Li, X., Liu, Y., Liu, Y., Novelli, A., Shao, M., Wang, H., Wu, Y., Zeng, L., Hu, M., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Wintertime photochemistry in Beijing: observations of RO_x radical concentrations in the North China Plain during the BEST-ONE campaign, *Atmos. Chem. Phys.*, 18, 12391-12411, <https://doi.org/10.5194/acp-18-12391-2018>, 2018.
- Tian, Y., Xue, Q., Xiao, Z., Chen, K., and Feng, Y.: PMF-GAS Methods to Estimate Contributions of Sources and Oxygen for PM_{2.5}, Based on Highly Time-Resolved PM_{2.5}

-
- Species and Gas Data, *Aerosol Air Qual. Res.*, 18, 2956-2966, <https://doi.org/10.4209/aaqr.2018.07.0244>, 2018.
- Wang, S., Yin, S., Zhang, R., Yang, L., Zhao, Q., Zhang, L., Yan, Q., Jiang, N., and Tang, X.: Insight into the formation of secondary inorganic aerosol based on high-time-resolution data during haze episodes and snowfall periods in Zhengzhou, China, *Sci. Total Environ.*, 660, 47-56, <https://doi.org/10.1016/j.scitotenv.2018.12.465>, 2019.
- Winer, A. M., and Biermann, H. W.: Long pathlength differential optical absorption spectroscopy (DOAS) measurements of gaseous HONO, NO₂ and HCNO in the California South Coast Air Basin, *Res. Chem. Intermed.*, 20, 423-445, <https://doi.org/10.1163/156856794X00405>, 1994.
- Zhang, B., and Tao, F.-M.: Direct homogeneous nucleation of NO₂, H₂O, and NH₃ for the production of ammonium nitrate particles and HONO gas, *Chem. Phys. Lett.*, 489, 143-147, <https://doi.org/10.1016/j.cplett.2010.02.059>, 2010.
- 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, *Sci. Total Environ.*, 648, 253-262, <https://doi.org/10.1016/j.scitotenv.2018.08.133>, 2019.