

Response to reviewer #1

General comments

The article “NH₃-promoted hydrolysis of NO₂ induces explosive growth in HONO” discussed the mechanism behind explosive HONO formation during field observation in a rural site in North China. In general, the phenomenon, confidence of related evidence were sufficient to show the role of NH₃ in HONO productions via heterogeneous reaction during fog/smoke events. The observation data was well linked to possible atmosphere processes, which might greatly promote the understanding of HONO sources and thus providing new insights of pollution control strategies for China. Yet, the authors should address several minor points to make the narrative as well as the deduction more convincing.

Minor suggestions

1. First, it is well known that the HONO is extremely reactive especially during daytime. For most of the cases, the author noted that the rarely seen Ozone was the evidence that there was no sufficient sunlight. It seems that the Ozone concentration was used as an indicator of UV radiation and possible photochemistry reactions (line213-line218). But the Ozone could be titrated by NO, which was often measured a high level during nighttime in North China. Therefore, even the Ozone was observed to be nearly zero, there might be enough UV radiation for the quick HONO photolysis. This leads to a further question - can we trust the HONO measurements by a denuder system? The annular denuder method of detecting might have artefacts regarding to measuring HONO due to: 1. Hydrolysis of NO₂ onto wet surface; 2. Aqueous reaction of S(IV) with NO₂ in the solution (Spindler, Hesper et al. 2003, Nie, Ding et al. 2015). The second reaction could likely be accelerated in the presence of ammonia as reported in the previous studies (Cheng, Zheng et al. 2016, Wang, Zhang et al. 2016). Therefore, it is strongly recommended that the authors should conducted some validation of the HONO data from IGAC,

given the fact that the HONO data obtained by denuder system need further calculation/reprocessing.

Response:

Thank you for your valuable comments. During the campaign in 2016, the IGAC instrument was borrowed from the Fortelice International Company. Unfortunately, circumstances do not allow us to borrow the instrument again for additional experiments, but we hope to prove the instrument reliable using the entire measurement dataset.

As already pointed out in your comment, instruments using wet denuders to collect gaseous HONO can cause sampling artefacts mainly via two pathways: 1) the NO₂ conversion on the surface of the sampling tube and the wet denuder and 2) the reaction of NO₂ with S(IV) in the absorption solution in wet denuder (Nie et al., 2015). The second pathway is avoided in IGAC by using a dilute (5×10^{-3} M) H₂O₂ solution, which quickly converts S(IV) to S(VI). The first artefact is often corrected for using a linear correction using slopes of 0.83-0.85. (Su, 2008; Qiang et al., 2014; Nie et al., 2015). Qiang et al. (2014) compared HONO measurements by an instrument called GAC-IC with that of LOPAP and found generally good agreement between both instruments after using a linear correction. Note that such linear adjustments do not alter the overall variation characteristics of HONO. The GAC and MARGA systems all consist of horizontally positioned wet denuders, in which the absorption solution might accumulate and cause additional artifacts. The IGAC system uses a vertically installed wet denuder, guaranteeing for the smooth outflow of the absorption solution. Overall, it is reasonable to believe that IGAC is able to capture the variation characteristics of HONO, even if a slope of 0.83 were used to correct the HONO data, the peaks would still reach 8.8, 7.9, 9.5 and 14.6 ppb, which is still very high.

Further, to prove that the observed peaks were not caused by instrument sampling artefacts, we analyzed the variation of observed HONO with SO₂, NO₂ and NH₃ during

15th Oct. to 25th Nov. 2016 (Fig.1). High HONO concentrations were typically observed under low SO₂ conditions, which proves that the sampling artefact due to the reaction of S(IV) and NO₂ in the wet denuder could be neglected. If the instrument would cause sampling artefacts due to NO₂ conversions, the high HONO concentrations should have been frequently observed under high NO₂ concentrations, which was not the case. The NO₂ concentrations at the occurrence time of the 4 peaks were all below 50 ppb. NO₂ often exceeded 50 ppb during the campaign, however, HONO stayed below 7 ppb throughout the whole campaign, except for the 4 cases studied in this work.

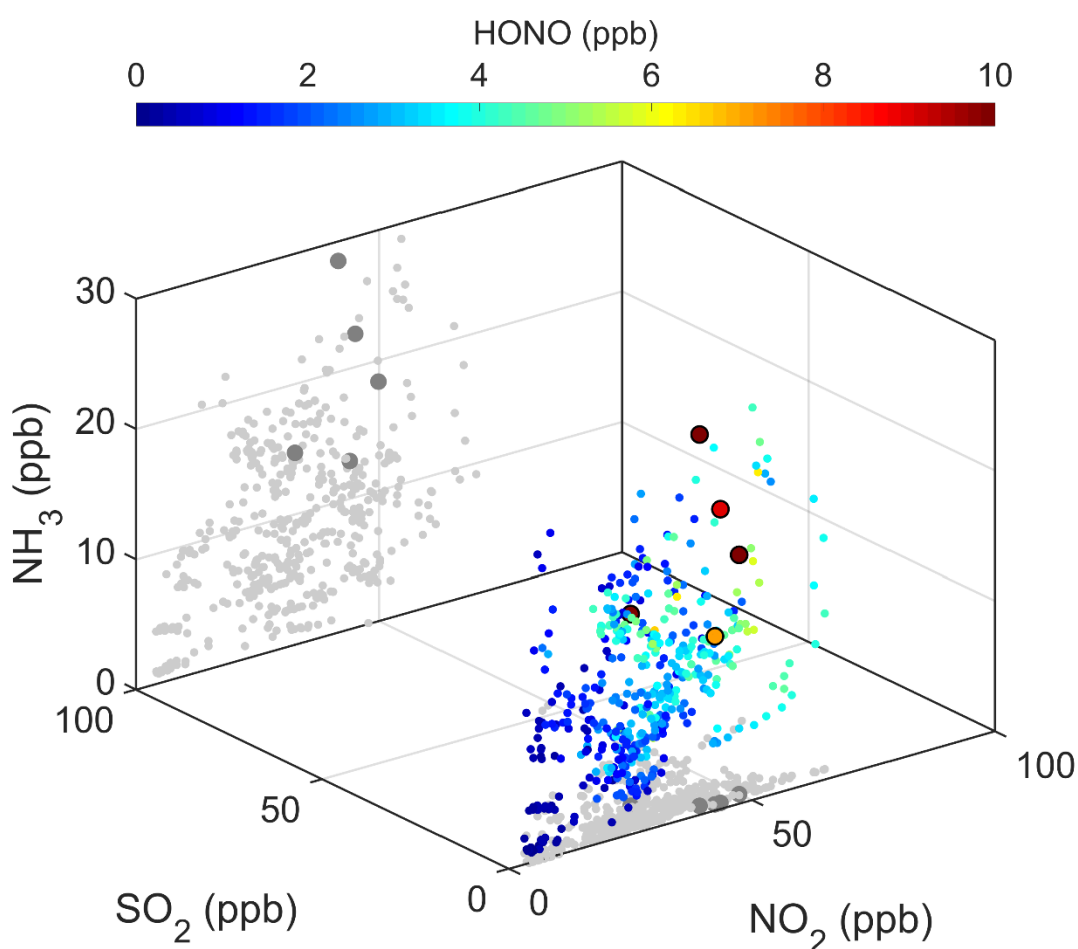


Figure 1 Variation of HONO with SO₂ (y-axis), NO₂ (x-axis) and NH₃ (z-axis) during 15th Oct. to 25th Nov. 2016, with the large dots indicating the data points with HONO exceeding 7 ppb

2. The second point will be lying in the mechanism discussions. Though R1 could not explain the increasing nitrate (line 260-261), but attributing all the SIA (secondary

inorganic aerosols) increase due to HONO formation and thus denying the role of R1 seems to be assertive. Actually, the nitrite in the aqueous phase might have produced OH radicals in aerosol liquid water or fog droplets (Vione, Maurino et al. 2006). It would be good to illustrate or maybe quantify the relative contribution of R1 v.s. R2 to HONO production as well as SIA production.

Response:

We thank the reviewer for these valuable comments and suggestions, which has greatly helped us in improving our manuscript. We took the advice in this comment and estimated the relative contributions of R1 and R2 to HONO production using the following assumptions.

First, we assume the observed increase in sulfate ($d[SVI]/dt$) was caused by the reaction of SO_2 with H_2O_2 , O_3 , NO_2 , TMI (Fe^{3+} and Mn^{2+}). Calculations were performed according to Cheng et al. (2016a), using the same pH dependent TMI concentrations and the actual SO_2 , H_2O_2 , O_3 and NO_2 concentrations in our measurements (Table 1). For the two fog episodes on 4th and 5th Nov. 2016, the mean diameter of fog droplets was assumed to be 7.0 μm and the liquid water content was assumed to be 0.3 $g\ m^{-3}$ according to Shen et al. (2018). For the haze episodes on the 11th and 14th Nov. 2016, the mean aerosol diameter under ambient conditions was estimated to be 0.65-1.22 and 0.9 μm , while the liquid water content was calculated to decrease from 3.4×10^{-4} to 7.8×10^{-5} on the 11th Nov and assumed to be 0.01 $g\ m^{-3}$ on the 14th Nov. during the transition from fog to haze. The sulfate production rate and relative contribution of the each oxidation pathway to the total sulfate production rate was obtained and depicted in Figure 2. For the two fog episodes, assuming pH=6, the estimated average sulfate production rates are 11.7 and 31.6 approximately 4 times of that observed within PM_{2.5}, which is clearly an underestimation, considering the liquid water content of fog droplets are at least a magnitude higher than that of aerosols. For the two haze episodes, using the pH values estimated using ISORROPIA (forward mode and metastable assumption (Song et al., 2018)), the estimated average sulfate production rates are 0.06 and 1.8,

about 10% of that observed within PM_{2.5}. Following the calculations of Cheng et al. (2016a), we have considered the influence of ionic strength on the reaction rates and set constraints on the maximum ionic strength (I_{max}), which might have caused underestimations for all reaction routes, since the calculated ionic strength commonly exceeded I_{max} . Underestimated transition metal ion concentrations may also be partly responsible for the underpredicted sulfate production, since the TMI catalysis route has recently be pointed out to be the dominant SO₂ heterogeneous oxidation pathway (Shao et al., 2019). Additionally, there also might be other neglected SO₂ oxidation pathways, which will lead to overestimates in the sulfate fraction produced by the NO₂ oxidation pathway.:

$$\frac{d[HONO]}{dt}_{R1} = 2 \times \text{frac}_{SO_2+NO_2} \times \frac{d[SVI]}{dt}_{obs}. \quad (1)$$

where $\text{frac}_{SO_2+NO_2}$ is the contribution fraction of the NO₂ oxidation pathway to the total sulfate production. Note that the calculated HONO production rate can only represent the production within PM_{2.5}.

Table 1. The trace gas concentrations, liquid water content, mean diameter and temperature used to calculate the heterogeneous sulfate production

Date	Time (LT)	SO ₂ (ppb)	H ₂ O ₂ (ppb)	NO ₂ (ppb)	O ₃ (ppb)	LWC (g m ⁻³)	D _p (μm)	T (K)
4 th Nov	9:00	0.18	0.26	45.3	1.53	0.3	7.00	277.8
	10:00	0.17	0.29	48.8	1.56	0.3	7.00	278.4
	11:00	0.28	0.34	49.9	1.78	0.3	7.00	278.7
5 th Nov.	10:00	0.16	0.19	44.6	2.90	0.3	7.00	278.8
	11:00	0.39	0.21	44.0	3.39	0.3	7.00	279.6
	12:00	1.19	0.30	45.1	5.72	0.3	7.00	281.3
11 th Nov.	7:00	0.40	0.52	30.7	1.41	3.4 e ⁻⁴	1.22	271.2
	8:00	0.44	0.71	33.0	1.53	2.1e ⁻⁴	0.73	272.3
	9:00	1.61	0.89	32.7	1.83	7.8e ⁻⁵	0.65	274.8
14 th Nov.	11:00	1.27	0.32	41.6	1.52	0.01	0.90	278.1

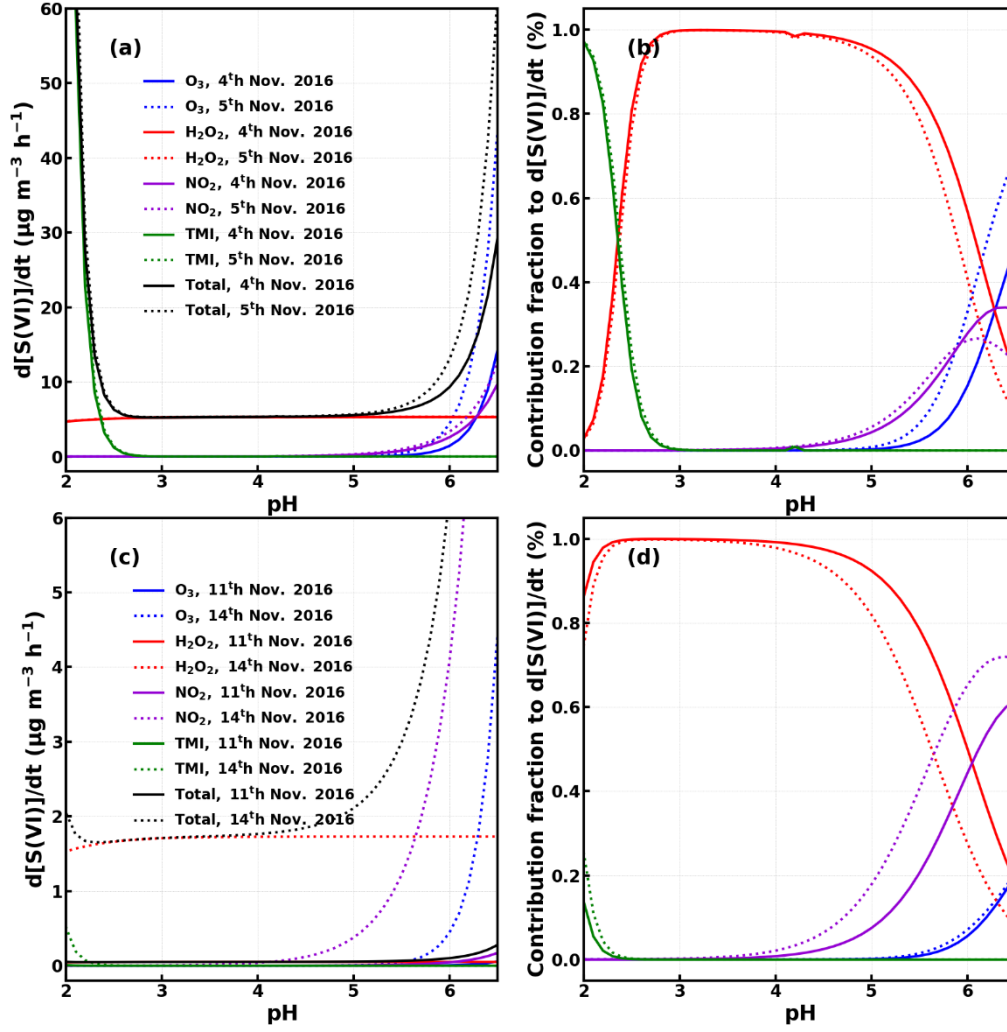


Figure 2. Calculated average sulfate production (a,c) and contribution fraction b,d) from SO_2 oxidation by H_2O_2 , NO_2 , O_3 , TMI under different pH values using methods described in (Cheng et al., 2016a) for the case episodes on 4th, 5th, 11th and 14th Nov. 2016.

Then, we further assume the observed nitrate production ($d[\text{NO}_3^-]/dt$) was caused by reaction R2 and by the reaction of NO_2 with OH radicals ($k_{\text{NO}_2+\text{OH}}=3.2\times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$), the HONO production rate of R2 would be:

$$\frac{d[\text{HONO}]}{dt}_{\text{R2}} = \frac{d[\text{NO}_3^-]}{dt}_{\text{obs}} - k_{\text{NO}_2+\text{OH}}[\text{NO}_2][\text{OH}]. \quad (2)$$

The contribution fraction of the two reactions to the heterogeneous HONO production in aerosol and fog liquid water content can be calculated by:

$$f_{\text{R1}} = \frac{d[\text{HONO}]}{dt}_{\text{R1}} / \frac{d[\text{HONO}]}{dt}_{\text{R1+R2}} \quad \text{and} \quad f_{\text{R2}} = \frac{d[\text{HONO}]}{dt}_{\text{R2}} / \frac{d[\text{HONO}]}{dt}_{\text{R1+R2}}.$$

Assuming the pH of fog droplets falls within the range of 4 to 6, f_{R2} was estimated to range from 75.5 to 99.5% and from 81.2 to 99.5% during the 4th and 5th Nov. 2016, respectively. For the two haze events on 11th and 14th Nov., the f_{R2} corresponding to the pH values modelled by ISORROPIA would be 98.2% and 97.3%.

These results suggest that, reaction R2 is the dominant contributor to the heterogeneous HONO production, while R1 is more important under high pH conditions. Under the assumed upper limit of pH, R1 can contribute up to 24.5%, 18.8% to the observed HONO growth during the fog events. This is in accordance with results from Wang et al. (2016) and Cheng et al. (2016b), which suggested that R1 was more likely to happen during fog episodes or under NH₃ neutralized conditions (3,4). For the two haze events, R1 contributed very little (1.8% and 2.7%) to the observed HONO growth.

In summary, reaction R2 was the dominant contributor to the heterogeneous HONO production, while R1 only played a minor role during fog events and a negligible role during haze events. The above discussions were added to Sect. 4.2 in the revised manuscript.

Technical notes

1. Line 110-111: “Under highly polluted conditions such as our site”. Might have wrong grammar used.

Response:

Thank you for noticing, this sentence was rephrased as:

“Considering the severe pollution state the NCP is under, these measurement uncertainties are fully acceptable.”

2. Figure 3. The time label on X axis causes misunderstanding, might change to Date-Time format.

Response:

Thank you for the suggestion, to avoid confusion the x axis labels were changed to hours and the date was marked on top of the figure (see Fig.4 below in Response #3).

3. Figure 4. The unit of aerosol composition (nitrate/sulfate/ammonium) should be in mass concentration.

Response:

Thank you for the suggestion, the unit of aerosol composition was changed to $\mu\text{g m}^{-3}$ in Figs. 2-4 (Figs. 3-5 below) and in the corresponding texts.

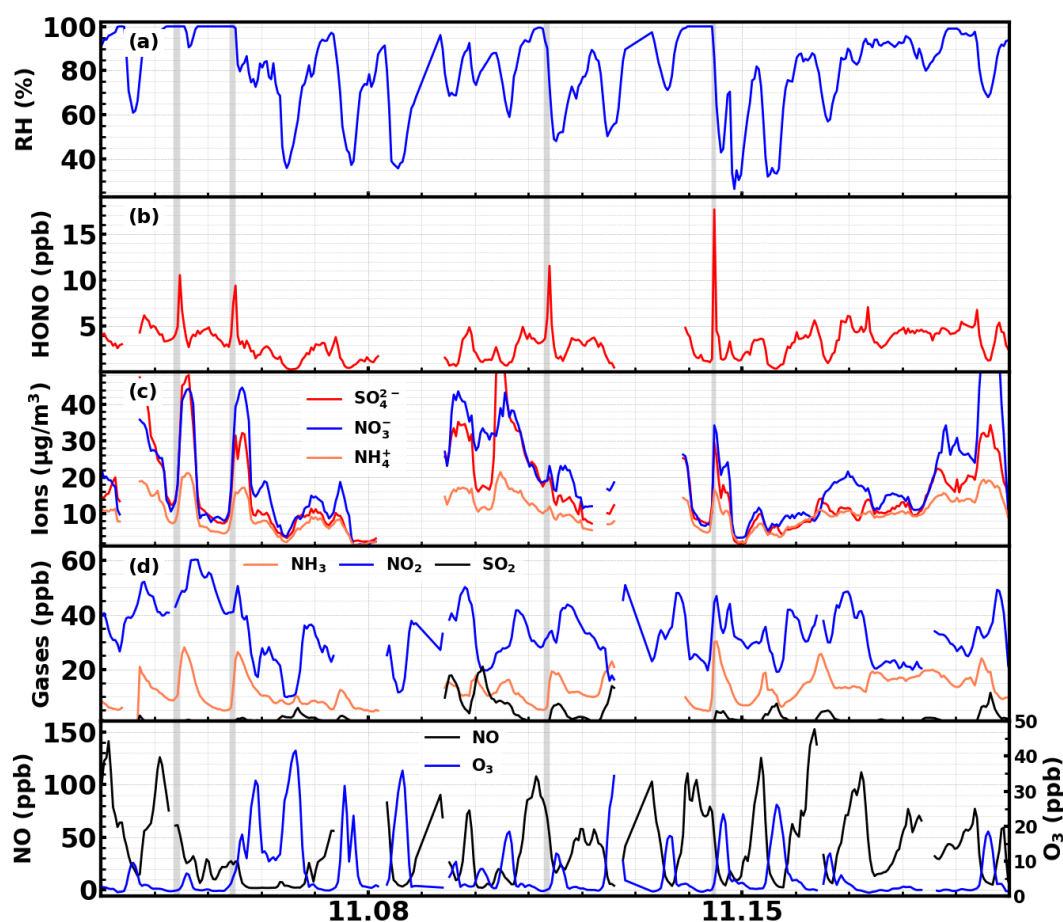


Figure 3. Time series of ambient **a)** RH; **b)** HONO; **c)** sulfate, nitrate, ammonium; **d)** NH_3 , NO_3 and SO_2 during the observation period.

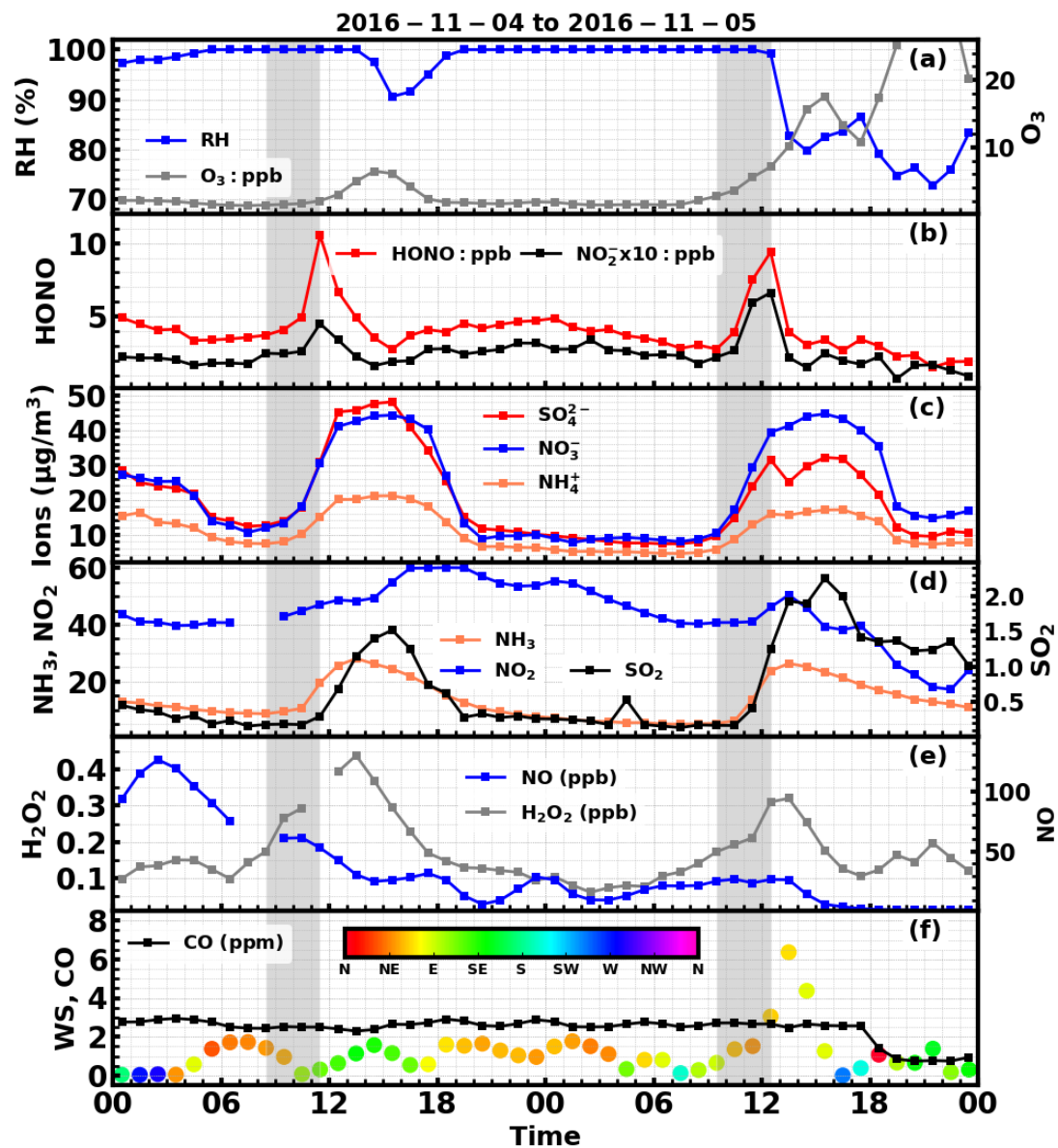


Figure 4 Time series of ambient a) RH, O_3 , b) HONO, NO_2 , c) SO_4^{2-} , NO_3^- , NH_4^+ , d) NH_3 , NO_2 , SO_2 , e) NO, H_2O_2 , f) CO, wind speed and wind direction (colors of scatter points) from 11-04 to 11-05. Gray shaded areas represent periods of rapid increase of HONO.

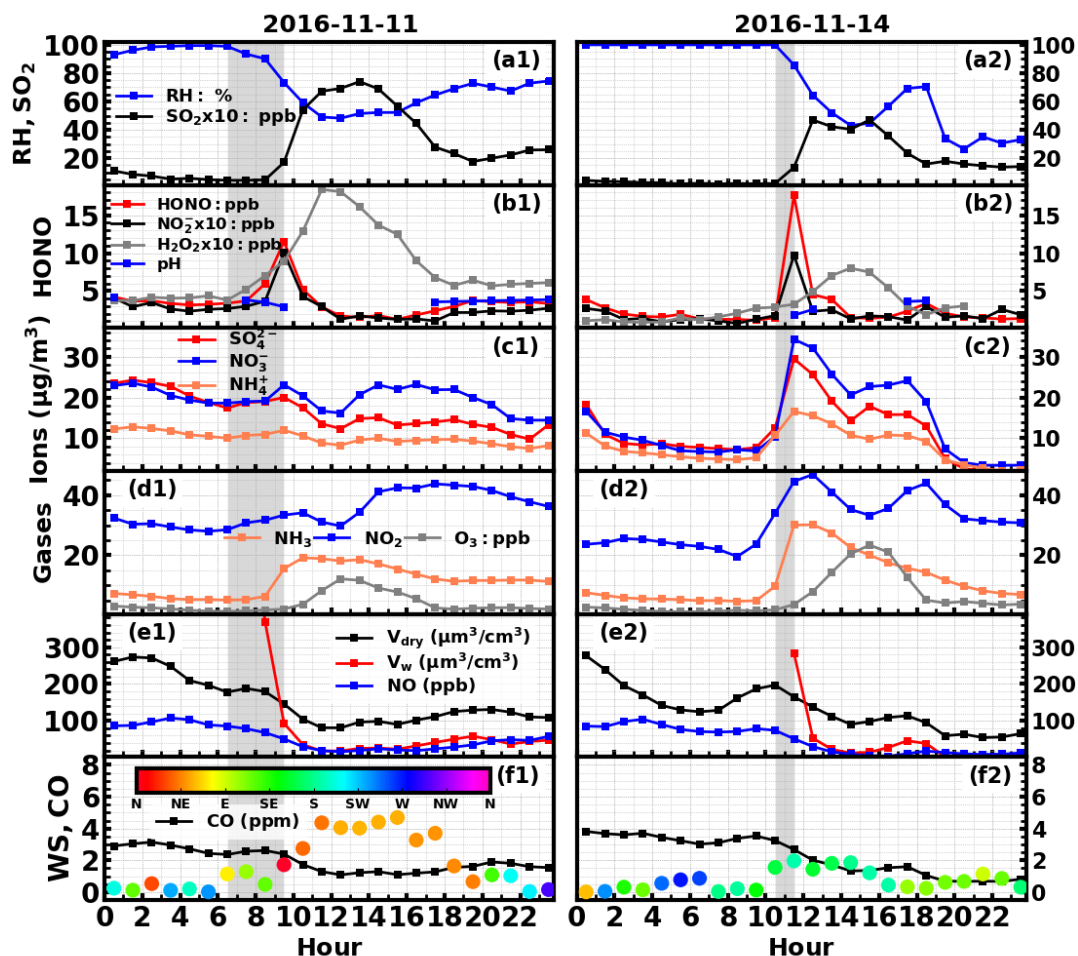


Figure 5 Time series of ambient **a)** RH, SO₂, **b)** HONO, NO₂⁻, H₂O₂, aerosol pH, **c)** SO₄²⁻, NO₃⁻, NH₄⁺, **d)** NH₃, NO₂, O₃, **e)** NO, volume concentrations of PM_{2.5} in dry state (V_{dry}), volume concentrations of liquid water (V_w), **f)** CO, wind speed and wind direction during **1)** 11th Nov. 2016 and **2)** 14th Nov. 2016. Gray shaded areas represents periods of rapid increase of HONO.

Reference

- Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, *Science Advances*, 2, e1601530, 10.1126/sciadv.1601530, 2016a.
- Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, *Science Advances*, 2, 10.1126/sciadv.1601530, 2016b.
- Nie, W., Ding, A. J., Xie, Y. N., Xu, Z., Mao, H., Kerminen, V. M., Zheng, L. F., Qi, X. M., Huang, X., Yang, X. Q., Sun, J. N., Herrmann, E., Petäjä, T., Kulmala, M., and Fu, C. B.: Influence of biomass burning plumes on HONO chemistry in eastern China, *Atmos. Chem. Phys.*, 15, 1147–1159, 10.5194/acp-15-1147-2015, 2015.
- Qiang, Y., Hang, S., Xin, L., YaFang, C., KeDing, L., Peng, C., JianWei, G., Song, G., Min, H., LiMin, Z.,

Tong, Z., and YuanHang, Z.: Daytime HONO formation in the suburban area of the megacity Beijing, China, *Science China(Chemistry)*, 57, 1032-1042, 2014.

Shao, J., Chen, Q., Wang, Y., Lu, X., He, P., Sun, Y., Shah, V., Martin, R. V., Philip, S., Song, S., Zhao, Y., Xie, Z., Zhang, L., and Alexander, B.: Heterogeneous sulfate aerosol formation mechanisms during wintertime Chinese haze events: Air quality model assessment using observations of sulfate oxygen isotopes in Beijing, *Atmos. Chem. Phys. Discuss.*, 2019, 1-28, 10.5194/acp-2018-1352, 2019.

Shen, C., Zhao, C., Ma, N., Tao, J., Zhao, G., Yu, Y., and Kuang, Y.: Method to Estimate Water Vapor Supersaturation in the Ambient Activation Process Using Aerosol and Droplet Measurement Data, *Journal of Geophysical Research: Atmospheres*, 123, 10606-10619, doi:10.1029/2018JD028315, 2018.

Su, H.: HONO: a study to its sources and impacts from field measurements at the sub-urban areas of PRD region, Peking University, Beijing, China, 2008.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, *Proceedings of the National Academy of Sciences*, 113, 13630, 2016.