RE：A point-to-point response to reviewers' comments

Referee comments are given in italic blank and the changes made to the manuscript are given in blue. The line numbers correspond to the revised new manuscript.

Reviewer #2

Fan et al present a revision of their manuscript reporting HCl and HBr observations in Beijing. The revisions made in response to reviewer comments significantly strengthened the manuscript. In particular, the reporting of uncertainties and LODs is important and useful. The move of now Figure 5 to the main text and associated caption and discussion edits are also excellent revisions that strengthen the manuscript. Similarly, the revisions to Figure 8 and added comparison of HCl and HBr on "clean" and polluted days are excellent.

Reply: We are very grateful for the positive comments. And we have carefully revised our manuscript accordingly. A point-to-point response to reviewers' comments (in italic), is given below.

I only have one remaining minor comment. It is not clear why the HCl and HBr concentrations represent lower limits (Line 257 of tracked changes version), as the reasoning for this is stated to be due to unquantified uncertainties such as different sensitivities to HCl and HBr, which reflect understanding of the value but not the directionality (lower/upper).

Reply: Thanks for the reviewer's suggestion. In the original expression, we would like to express that the HBr concentrations should be treated as semi-quantified ones regarding to the charging of reagent ions. The reason is as follows:

Ideally, the concentration of HBr could be quantified by the HBr calibration coefficient multiplying the normalized Br^- signals by total reagent ions (i.e., NO_2^-, O_2^- and NO_3^-), which is shown in equation 1 (E1):

$$[HBr] = C_{HBr} \times \frac{(Br^-)}{(NO_2^-) + (O_2{}^-) + (NO_3^-)} \qquad \text{E (1)}$$

where [HBr] is the concentration of HBr and C_{HBr} is the calibration coefficient of HBr. (Br^-), (NO_2^-), (O_2^-), (NO_3^-) represent the signals of Br^-, NO_2^-, O_2^- and NO_3^- from CI-APi-LTOF, respectively.

Since the HBr calibration coefficient was absent, we applied the calibration coefficient of HCl (C_{HCl}) achieved from the inter-comparison between MARGA and CI-APi-LTOF as an alternative of C_{HBr} to semi-quantify HBr (E2).

$$[HBr] = C_{HCl} \times \frac{(Br^-)}{(NO_2^-) + (O_2{}^-) + (NO_3^-)} \qquad \text{E (2)}$$

However, considering the fraction of the cluster of $HBr \cdot NO_3^-$ (or $Br^- \cdot HNO_3$) to total Br- was less than 4%, the reaction pathway of HBr with NO_3^- was not considered. Therefore, the HBr was quantified by the equation 3 (E3):

$$[HBr] = C_{HCl} \times \frac{(Br^-)}{(NO_2^-) + (O_2{}^-)} \qquad \text{E (3)}$$

Thus, the presented HBr concentrations should be treated as semi-quantified ones.

We have revised the statements in the manuscript accordingly to minimize the potential misunderstanding (line number correspond to revised MS):

Line 251-254: "Similar to HCl, the same uncertainty was also adopted for HBr mixing ratios. It should be noted that our assumptions lead towards a lower limit estimate of HCl and HBr concentrations, due to other potential uncertainties (e.g., different sensitivities of HCl and HBr) were not taken into account." has been revised. We also correct the typo in Line 254. The revised statement is as follows:

"Similar to HCl, the same uncertainty was also adopted for HBr mixing ratios. It should be noted that our assumptions lead towards a semi quantitative estimation of HBr concentrations, due to other potential uncertainties (e.g., different sensitivities of HCl and HBr) were not taken into account."

Line 268-269: "The presented HBr concentrations should be treated as semi-quantification ones and upper limit values." has been revised to "The presented HBr concentrations should be treated as semi-quantitative ones".

Reviewer #3

This is an interesting study presenting new measurements of HCl and HBr in Beijing. I only have a few minor comments that the authors should consider addressing.

Reply: We are very grateful for the positive comments and have carefully revised our manuscript accordingly.

1. Use of [NO_2*][OH] as proxy for* HNO_3

Line 316. "HNO_3 *which was indicated as [*NO_2*]*[OH]" I don't understand this statement. Are the authors measuring* NO_2*, calculating OH, and then assume that the product of the two is proportional to* HNO_3*? This doesn't seem correct.* NO_2*+OH is certainly one pathway for* HNO_3 *production, the other being heterogeneous reaction of* N_2O_5 *on aerosols, which is likely quite important in winter. Furthermore, the lifetime of* HNO_3 *is much longer than that of* NO_2 *or OH, so the product of [*NO_2*][OH] might not be a good proxy for the actual* HNO_3 *concentrations. It might be more useful to plot* NO_2 *and OH separately on figure 3.*

Reply: We agree with the reviewer that the reaction of NO_2 and OH is not the only pathway for HNO_3. The concentrations of NO_2 and OH were based on direct measurement and calculation, respectively (Section S8 in SI). However, NO_2+OH reaction would be one of the dominant pathways of HNO_3 during the daytime when elevated HCl and HBr were observed. In a previous study, this reaction is also regarded to be the largest sink of NO_x globally (Stavrakou et al., 2013). The formation pathways of gaseous HNO_3 from the heterogeneous reactions of N_2O_5 would be much more important during the night time, especially during the haze periods (Wang et al., 2020).

We did notice that the lifetime of HNO_3 could be longer than NO_2 or OH (Amedro et al., 2020; Hanke et al., 2003), which may result in uncertainties in HNO_3 estimations. Considering those factors mentioned above, we toned down the expression of NO_2, OH and their product in the main text and separately exhibit [NO_2] and [OH] in Figure 3 as suggested.

To make our statement clear, we revised the manuscript accordingly:

Line 316-321:

From: "Figure 4d, it also can be found that elevated temperature and high abundance of HNO_3 which was indicated as [NO_2]*[OH] could intensify the HCl releases from particulate chloride in the daytime from 08:00 to 17:00."

To: "From Figure 4d, it also can be found that elevated HCl is associated with high temperature and [NO_2]*[OH] value. Considering the reaction of NO_2 with OH radical is one of the dominant formation pathways of gaseous HNO_3 during the daytime (Stavrakou et al., 2013), it implies that strong photochemical reactions and the following potential elevated HNO_3 could intensify the HCl releases from particulate chloride in the daytime from 08:00 to 17:00."

According to the suggestions, we revised Figure 3 (Figure R1) as shown.

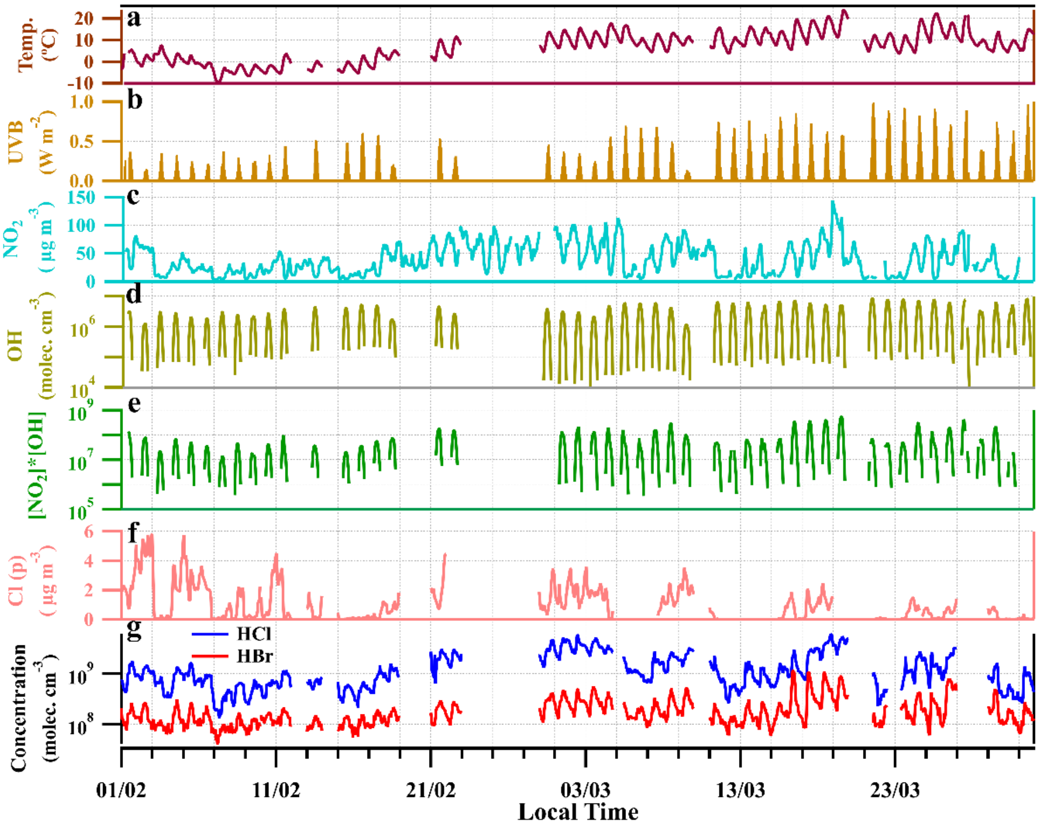

Figure R1 (Figure 3 in main text). Time profiles of temperature (**a**), UVB intensities (**b**), NO_2 concentration (**c**), OH concentration from calculation (**d**), $[NO_2]*[OH]$ ($\mu g\ m^{-3}$ * molecules cm^{-3}) (**e**), particulate chloride concentration (Cl(p)) (**f**) and the mixing ratios of HCl and HBr (**g**). The data points are in hourly-average interval.

2. OH calculation

Line 315 and supplemental info. The method and justification for calculating OH is not very clear. It seems that it is based on J_{O1D} and NO_2 measurements and based on inferred JNO_2. S8 cites 2 papers: Xu et al. and Tan et al. It is unclear whether the empirical fit from Xu et al. (2015) in equation S2 was originally obtained from observations of OH concentrations or model calculations. Also, the authors then go on to say (SI, lines 359-365), that they use the results from Tan et al. (2018), which they mention is only a function of J_{O1D}. Can the authors clarify the whole section? What equation do they use (the one from Xu or from Tan)? What is that equation based on? Pure model calculations (and if so, what are the main sources of OH?) or actual observations of OH?

Reply: Thanks for reviewer's comment. In this study, we applied the empirical equation ($[OH] = J_{O1D}\times2\times10^{11}$) from Tan et al., 2019 to estimate the OH concentrations, which is proposed by the direct OH measurement by LIF (Laser-Induced Fluorescence) in the North China Plain region. We then applied a more detailed calculation proposed by Xu et al., 2015 to validate the calculation. Comparable results were achieved from these two methods in both concentration levels and diel patterns (as shown in Figure S11). There is a typo in the text (Line 363), the citation should be "Tan et al., (2019)" and has been corrected through the entire SI.

To make the OH calculation method clear, we revised the supplemental accordingly (line number correspond to revised SI):

Line 355-369:

"In this work, there is no direct measurement of OH radical concentration during observation periods. While during the winter and spring in Beijing, it has been found that the measured OH radical concentration is linearly correlated with photolysis rate of ozone, J_{O1D} (Liu et al., 2020; Tan et al., 2019). Thus, an empirical equation was proposed to estimate the OH concentrations: [OH] = $J_{O1D}\times2\times10^{11}$ molecules cm^{-3}. We adopted this empirical equation to calculate the OH concentration in this study.

We further validated our calculation by comparing the OH concentration, obtained with another method suggested by Xu et al. 2015 (Xu et al., 2015), which considering both photolysis rate (J_{O1D} and J_{NO_2}) and NO_2 concentration (C_{NO_2}) based on formula equation (S2). Using another dataset collected from 21 May to 10 June 2019 where the parameters of J_{NO_2} and C_{NO2} were available from direct measurements, a good correlation (r=0.97) was achieved between measured J_{NO_2} and predicted J_{NO_2} which was derived from the solar zenith angle and the location using a box model (FACSIMILE 4) (Liu et al., 2020), confirming the validation of our predicted J_{NO_2} (Figure S11a)."

$$c_{OH} = \frac{4.1\times10^{9}\times(J_{O1D})^{0.83}\times(J_{NO_2})^{0.19}\times(140c_{NO_2}+1)}{0.41c_{NO_2}^{2}+1.7c_{NO_2}+1} \qquad \text{Eq. (S2)}$$

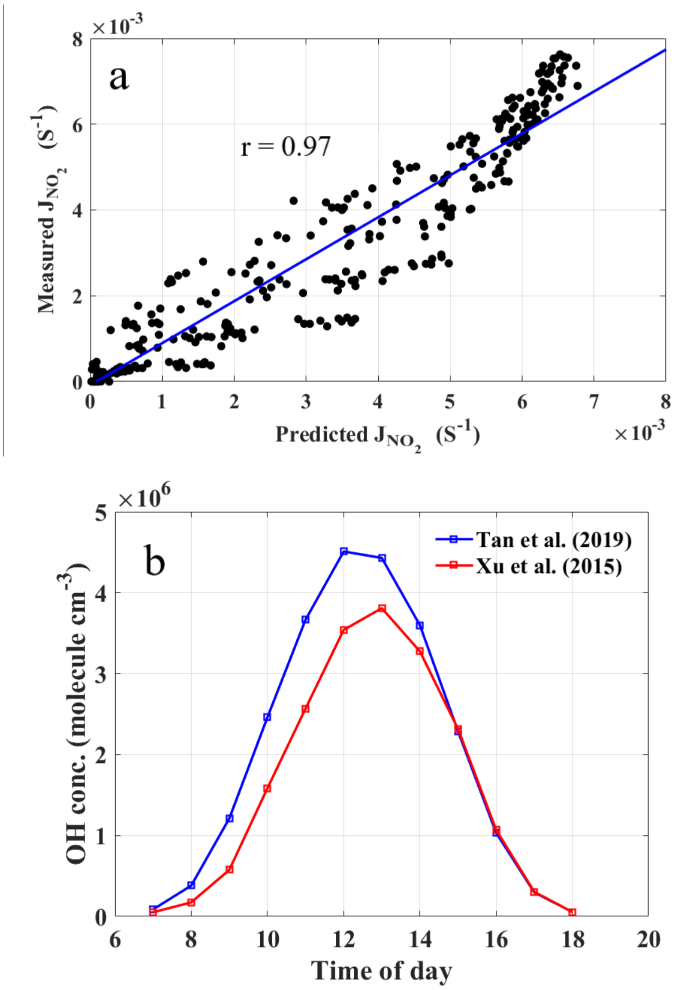

Figure R2 (Figure S11). High correlation (r = 0.97) between measured and predicted J_{NO_2} from 21 May to 10 June 2019 (**a**); Calculated diurnal curve of OH concentration based on Tan et al., (2019) and Xu et al., (2015) from 1 February to 31 March 2019 (**b**).

Additional Comments:

Page 4 line 187: "is of necessary" should be replaced with "is necessary"

Reply: "is of necessary" has been changed to "is necessary" in the manuscript.

Page 6 260 "due to a direct calibration for HBr" should be replaced with "as direct calibration for HBr"

Reply: It has been revised accordingly.

Line 268 "semi-quantification" should be replaced with "semi quantitative" as direct calibration for HBr

Reply: It has been changed accordingly throughout the manuscript.

Figure 5. The figure is difficult to read with different units plotted molec/cm^3, mol/mol, ug/m^3. I suggest that the authors stick to one unit: pptv. Given that the point of the figure is to look at

the ratio between HCl and pCl this will make the figure more straightforward to read. Also, the panel on the right has 2 y axis with Cl(p) and none with HCl.

Reply: Thank you for the suggestion. We agree that it is difficult to read with different units in the plot. By considering the consistency of the unit of manuscript in Figure 4 of the main text, we prefer to use the unit as "molecules cm^{-3}" for concentration of gas-phase species and "µg m^{-3}" for concentration of particulate compounds. Meanwhile, we also added the following Figure R3 in pptv to the SI (Figure S13 in the revised SI) as suggested by the reviewer to help the readers to compare with previous studies using the unit of pptv.

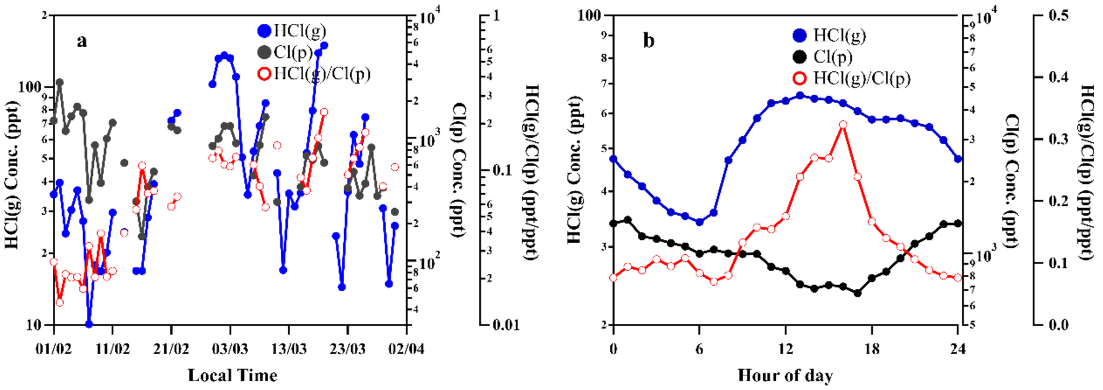

Figure R3 (Figure S13 in SI). Time variation of daily averaged concentration of particulate chloride (Cl(p)) measured by ACSM, gaseous HCl (HCl(g)) measured by CI-APi-LTOF and mole ratios of HCl(g)/Cl(p) (a) and diurnal variation of HCl(g), Cl (p) and mole ratios of HCl(g)/Cl(p) (b). Note that the plots are similar to those in Figure 5 of the main text, but this is displayed as pptv.

The typo in Figure 5 panel b on the left y-axis has been corrected to "HCl (g) Conc. (molec. cm^{-3})" shown as Figure R4.

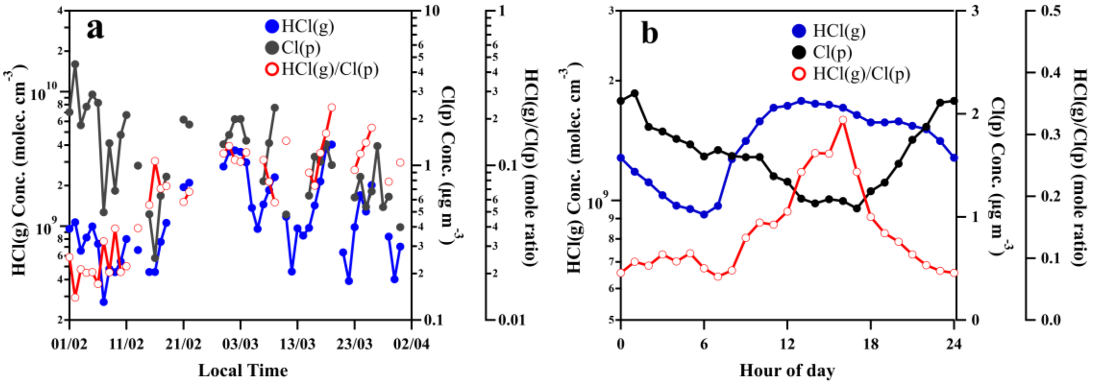

Figure R4 (Figure 5 in main text). Time variation of daily averaged concentration of particulate chloride (Cl(p)) measured by ACSM, gaseous HCl (HCl(g)) measured by CI-APi-LTOF and mole ratios of HCl(g)/Cl(p) (**a**) and diurnal variation of HCl(g), Cl (p) and mole ratios of HCl(g)/Cl(p) (**b**).

Text unclear as to whether the HBr values reported are upper or lower limits. Line 252 "lower limit estimates" while line 268 states "HBr concentrations should be treated as semi-quantification ones and upper limit values".

Reply: Thank you for the suggestion. Please refer to our reply for the comment from reviewer#2. For the convenience, the reply was copied below:

In the original expression, we would like to express that the HBr concentrations should be treated as semi-quantified ones regarding to the charging of reagent ions. The reason is as follows:

Ideally, the concentration of HBr could be quantified by the HBr calibration coefficient multiplying the normalized Br^- signals by total reagent ions (i.e., NO_2^-, O_2^- and NO_3^-), which is shown in equation 1 (E1):

$$[HBr] = C_{HBr} \times \frac{(Br^-)}{(NO_2^-)+(O_2{}^-)+(NO_3^-)} \qquad \text{E (1)}$$

where [HBr] is the concentration of HBr and C_{HBr} is the calibration coefficient of HBr. (Br^-), (NO_2^-), (O_2^-), (NO_3^-) represent the signals of Br^-, NO_2^-, O_2^- and NO_3^- from CI-APi-TOF, respectively.

However, since the HBr calibration coefficient was absent, we applied the calibration coefficient of HCl (C_{HCl}) achieved from the intercomparison between MARGA and CI-APi-LTOF as an alternative of C_{HBr} to semi-quantify HBr (E2).

$$[HBr] = C_{HCl} \times \frac{(Br^-)}{(NO_2^-)+(O_2{}^-)+(NO_3^-)} \qquad \text{E (2)}$$

However, considering the fraction of the cluster of $HBr{\cdot}NO_3^-$ (or $Br^-{\cdot}HNO_3$) to total Br- was less than 4%, the reaction pathway of HBr with NO_3^- was not considered. Therefore, the HBr was quantified by the equation 3 (E3):

$$[HBr] = C_{HCl} \times \frac{(Br^-)}{(NO_2^-)+(O_2{}^-)} \qquad \text{E (3)}$$

Thus, the presented HBr concentrations should be treated as semi-quantified ones.

We have revised the statements in the manuscript accordingly to minimize the potential misunderstanding (line number correspond to revised MS):

Line 250-253: "Similar to HCl, the same uncertainty was also adopted for HBr mixing ratios. It should be noted that our assumptions lead towards a lower limit estimate of HCl and HBr concentrations, due to other potential uncertainties (e.g., different sensitivities of HCl and HBr) were not taken into account." has been revised. We also correct the typo in Line 254. The revised statement is as follows:

"Similar to HCl, the same uncertainty was also adopted for HBr mixing ratios. It should be noted that our assumptions lead towards a semi-quantitative estimation of HBr concentrations, due to other potential uncertainties (e.g., different sensitivities of HCl and HBr) were not taken into account."

Line 267-268: "The presented HBr concentrations should be treated as semi-quantification ones and upper limit values." has been revised to "The presented HBr concentrations should be treated as semi-quantitative ones".

References:

Amedro, D., Berasategui, M., Bunkan, A. J. C., Pozzer, A., Lelieveld, J., and Crowley, J. N.: Kinetics of the OH + NO_2 reaction: effect of water vapour and new parameterization for global modelling, Atmospheric Chemistry and Physics, 20, 3091-3105, 10.5194/acp-20-3091-2020, 2020.

Hanke, M., Umann, B., Uecker, J., Arnold, F., and Bunz, H.: Atmospheric measurements of gas-phase HNO_3 and SO_2 using chemical ionization mass spectrometry during the MINATROC field campaign 2000 on Monte Cimone, Atmos. Chem. Phys., 3, 417-436, 10.5194/acp-3-417-2003, 2003.

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, 10.5194/acp-20-13023-2020, 2020.

Stavrakou, T., Müller, J. F., Boersma, K. F., van der A, R. J., Kurokawa, J., Ohara, T., and Zhang, Q.: Key chemical NOx sink uncertainties and how they influence top-down emissions of nitrogen oxides, Atmospheric Chemistry and Physics, 13, 9057-9082, 10.5194/acp-13-9057-2013, 2013.

Tan, Z., Lu, K., Jiang, M., Su, R., Zhang, Y.: Daytime atmospheric oxidation capacity in four Chinese megacities during the photochemically polluted season: A case study based on box model simulation. Atmospheric Chemistry and Physics 19, 3493-3513,2019.

Wang, Y., Chen, Y., Wu, Z., Shang, D., Bian, Y., Du, Z., Schmitt, S. H., Su, R., Gkatzelis, G. I., Schlag, P., Hohaus, T., Voliotis, A., Lu, K., Zeng, L., Zhao, C., Alfarra, M. R., McFiggans, G., Wiedensohler, A., Kiendler-Scharr, A., Zhang, Y., and Hu, M.: Mutual promotion between aerosol particle liquid water and particulate nitrate enhancement leads to severe nitrate-dominated particulate matter pollution and low visibility, Atmospheric Chemistry and Physics, 20, 2161-2175, 10.5194/acp-20-2161-2020, 2020.

Xu, Z., Wang, T., Wu, J., Xue, L., Chan, J., Zha, Q., Zhou, S., Louie, P.K.K., Luk, C.W.Y.: Nitrous acid (HONO) in a polluted subtropical atmosphere: Seasonal variability, direct vehicle emissions and heterogeneous production at ground surface. Atmospheric Environment 106, 100-109, 2015.