

Reviewer1

This study systematically evaluates the interferences of atmospheric trace gases on HONO measurements by using the prevailing WD/IC technique through comparison with the LOPAP technique that is currently believed to be one of the reliable techniques for HONO measurements. The results and conclusions of the manuscript seem to be convincing and the method established for correcting HONO concentrations measured by the WD/IC technique is useful to calibrate the large database measured in the past and ongoing data. This reviewer recommends the manuscript to be published in the journal after considering following specifics:

[Response: we thank the reviewer for the comments and suggestions. We have revised the manuscript accordingly and addressed the specific comments as follows.](#)

1. Lines 49-52, the chemical method of stripping coil-ion chromatograph is suggested to be included, e.g., Cheng et al., 2013, J. Environ. Sci. (Chinese) 25, 895-907; Xue et al., 2019, Science of the total Environment, 646: 187-195; 659: 621-631.

[Response: Thanks for the information, and these reference have been added into the revised manuscript.](#)

2. 2.2 Instrumentation: The length of inlet tube for both the MARGA and LOPAP is suggested to be mentioned because serious interference of the inlet tube may be important as you mentioned in the introduction.

[Response: Only 1-2cm inlet of LOPAP was in front of sample box, which is one the major advantage of LOPAP compared to other HONO measurement techniques. The length of MARGA`s inlet is 3 meter. We have added the information in the revised manuscript.](#)

[Modify: “MARGA was located in the top floor of the laboratory building with the sampling inlet of 3m.”](#)

3. Lines171-175, the description of the two sentences is not clear, and suggested to be rephrased as “The average diurnal variations of HONO marga and HONO lopap, as shown Figure 1b, HONO marga /HONO lopap ratios were higher at night, and especially in the morning, which were different from the results of Muller et al. (1999) who found the

remarkable overestimation of HONO by WD/IC usually occurred during daytime.”.

Response: Thanks for the correction. This sentence has been rephrased accordingly in the revised manuscript.

4. Lines 175-177, “Meanwhile, the correlation between the HONO concentrations measured by WD/IC and other measured HONO concentrations varied in different studies.” is suggested to be replaced by “Meanwhile, the correlations between the HONO concentrations measured by WD/IC and by another techniques varied in different studies”. This sentence seems to be meaningless, can be deleted.

Response: Thanks for the correction. This sentence has been rephrased accordingly in the revised manuscript.

5. Lines 177-181, “In our study, the slope of HONO lopap to HONO marga was approximately 0.57, with a correlation coefficient  $r^2=0.3$ . Combined with the limited comparison study on HONO concentrations measured by a WD/IC instrument and LOPAP (Lu et al., 2010; Ramsay et al., 2018), the slope at the four sites varied from 0.32 to 0.87. The large variation may indicate that the performance of WD/IC in the measurement of HONO is environmental dependent” is suggested to be replaced by “the slope of HONO lopap to HONO marga measured by this study was approximately 0.57 (with a correlation coefficient of  $r^2=0.3$ ) which was within the large range of 0.32-0.87 reported by the limited comparison investigations on HONO measurements using a WD/IC instrument and LOPAP at four sampling sites (Lu et al., 2010; Ramsay et al., 2018). Such large variation of the slopes at the different sampling sites may indicate that the performance of WD/IC in the measurement of HONO is environmental dependent”. In addition, a brief introduction of the difference for the environments at the different sites is needed, or the conclusion is farfetched.

Response: Thanks for the correction. These statements have been modified accordingly in the revised manuscript. We have added additional information to describe the sites.

6. Lines 185-187, “As the major precursor of HONO, the heterogeneous reaction of NO<sub>2</sub> on the sampling tube or aerosol may introduce the artificial HONO” should be “As the potential source for HONO, the heterogeneous reaction of NO<sub>2</sub> on the sampling tube or

aerosol may introduce the artificial HONO”.

Response: Thanks for the correction. This sentence has been modified accordingly in the revised manuscript.

7. Lines 192-194, the phenomenon described by “Compared to HONOlopap, HONOmarga was significantly higher at a high concentration of SO<sub>2</sub> and had the opposite trend at a high concentration of ammonia” is inconsistent with Figure 2 and the following discussions. According to the illustration of Figure 2, HONOmarga was much higher than HONOlopap under lower SO<sub>2</sub> concentrations and higher NH<sub>3</sub> concentrations, and vice versa.

Response: Thanks. This is a typo, and has been corrected in the revised manuscript.

“Compared to HONOlopap, HONOmarga was significantly lower at a high concentration of SO<sub>2</sub> and had the opposite trend at a high concentration of ammonia”

8. Lines 230-231, are the 13 samples collected from the atmosphere, or specially prepared? It is difficult to understand the large range of pH values (from 0-14) for actual air samples. The authors are suggested to present the detail information about it. The reliability for calculating the pH of solution by using Curtipot has been intensively tested for developing the model, and hence, the further verification is not necessary in here (the paragraph and the corresponding figures are suggested to be deleted).

Response: Yes, the 13 samples was specially prepared. The different concentration SO<sub>2</sub> concentration was added into the samples tube together with ambient air with about 13 ppbv NH<sub>3</sub>, to adjust the pH of denuder liquid.

“In order to adjust the pH of denuder solution, SO<sub>2</sub> with concentration of 0, 5, 10, 20, 40, 80 and 100 ppbv were injected into the sampling line with the NH<sub>3</sub> concentration around 10-15 ppbv.”

9. Lines 251-254, these conclusions are not rigorous, because breakthrough of HONO can also occur for LOPAP. The authors are suggested to reveal the collection efficiencies’ range of HONO by Marga during actual measurements to support the statement of 200% HONO underestimation in the lowest pH in the abstract.

Response: To improve HONO collection efficiency, the stripping solution of LOPAP

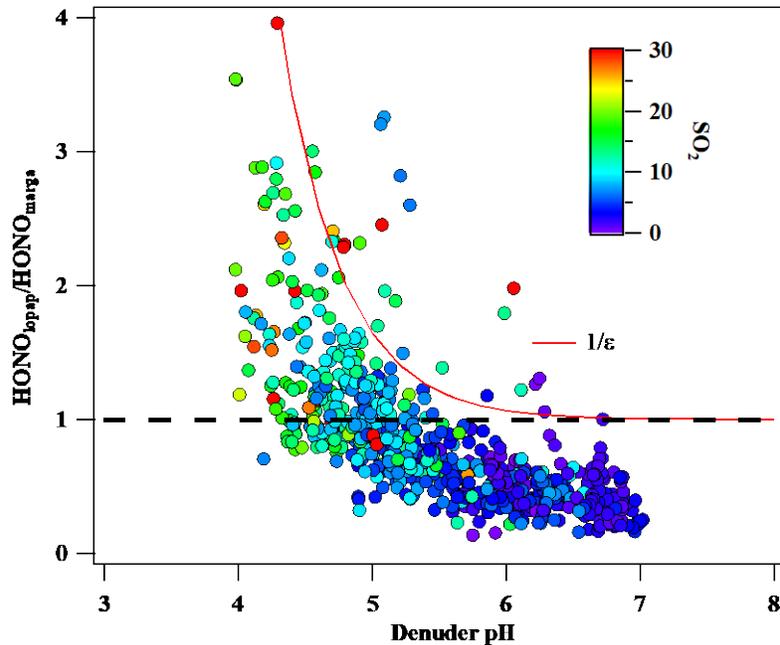
contains 0.06 M sulfanilamide in 1M HCl which immediately forms a diazonium salt with HONO. This guarantee the sampling efficiency of LOPAP to be 100 % and independent of the atmospheric composition due to the very fast chemical reaction (Kleffmann and Wiesen, 2008; Heland et al., 2001).

In our study, the HONO collection efficiency of MARGA was estimated by the following Eq.1 and Eq.2

$$\varepsilon = \frac{f_a}{f_g/H_{eff}+f_a} \quad (Eq.1)$$

$$H_{eff} = H(1 + \frac{K_a}{H^+}) \quad (Eq.2)$$

According to the Eq.1 and Eq.2 variation of HONO collection efficiency with pH was shown in Fig.3. Actually 200% HONO underestimation was resulted from Fig4. In the pH of 4-4.5 with low HONO collection efficiency, HONO<sub>lopap</sub>/HONO<sub>marga</sub> was about 3. Here, there was a typo in this Fig 4, that the red line should be the reciprocal of collection efficiency (1/ε) instead of collection efficiency. We have corrected this mistake in the revised manuscript.



Variation in the ratio of HONO<sub>lopap</sub> to HONO<sub>marga</sub> with the denuder absorption solution pH. The red line is the reciprocal of the HONO collection efficiency of MARGA.

Reference:

Heland, J., Kleffmann, J., Kurtenbach, R., and Wiesen, P.: A New Instrument To Measure Gaseous Nitrous Acid (HONO) in the Atmosphere, *Environmental Science & Technology*, 35, 3207-3212, 10.1021/es000303t, 2001.

Kleffmann, J., and Wiesen, P.: Technical Note: Quantification of interferences of wet chemical HONO LOPAP measurements under simulated polar conditions, *Atmos. Chem. Phys.*, 8, 6813-6822, 10.5194/acp-8-6813-2008, 2008.

10. Lines 254-256, this sentence is meaningless, can be deleted.

Response: We have deleted this sentence in the revised manuscript.

11. Lines 268-274, these sentences can be concise, e.g., the sentence of “Therefore, a correlation ...” can be deleted; the small fraction of NO<sub>2</sub> hydrolysis for HONO formation can be compared with the previous study in one sentence.

Response: Thanks for the comments. We have rephrased the statements in the revised manuscript.

“In the study by Spindler et al. (2003), approximately 0.058% of NO<sub>2</sub> was hydrolyzed to HONO, suggesting a small contribution of NO<sub>2</sub> hydrolysis the artificial HONO in the denuder solution. In this study, a similar ratio (0.060%) was found at a low PH (<4.5) (this part is discussed in the below section).”

12. Lines 282-283, The explanation is not clear.

Response: We have rewritten this part in the revised manuscript.

“This discrepancy with the study of Spindler et al. (2003) should be due to the additional H<sub>2</sub>O<sub>2</sub> in MARGA’s denuder solution competitive oxidizing SO<sub>2</sub>.”

13. Lines 284-285, the competition (“complete SO<sub>2</sub> oxidation” in your text may mistyped) oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> and NO<sub>2</sub> in the atmosphere can be dated back in 1980s, is not original finding from Cheng et al.

Response: Thanks for the comments. We have modified the statement and reference in the

revised manuscript.

“The competition of SO<sub>2</sub> oxidation by H<sub>2</sub>O<sub>2</sub> and NO<sub>2</sub> in the atmosphere has been well studied (Hoffmann and Calvert, 1985; Seinfeld and Pandis, 2016)”

14. Line 286, “a similar oxidation process” should be “the similar competition oxidation process”.

Response: We have modified the statement accordingly.

15. Lines 309-315, the equilibrium of HSO<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>-</sup>, SO<sub>2</sub> in liquid should be very fast, the fast oxidation of HSO<sub>3</sub><sup>-</sup> by H<sub>2</sub>O<sub>2</sub> will be quickly compensated by a new equilibrium even under high pH values, e.g., the sulfate formation rate is almost independent of pH values through H<sub>2</sub>O<sub>2</sub> oxidation. Figure 6b illustrated may be in correct because the shift of the equilibrium of sulfur species in the liquid is not considered. In addition, the liquid oxidation of SO<sub>2</sub> by O<sub>2</sub> also account for large fraction under basic condition, the nearly 100% sulfur oxidation by NO<sub>2</sub> at pH of 8 is not proper

Response: The condition in MARGA system is different from that in the ambient air. In the following figure, we showed the concentration and distribution of S(IV) species as a function of solution pH for the condition of 1ppb SO<sub>2</sub> in the ambient air. The oxidation rate of S by H<sub>2</sub>O<sub>2</sub> in the liquid phase would follow the equation (Eq. 3). In the ambient air, SO<sub>2</sub> and S(IV) in the aerosol phase are always assumed to be in the equilibrium, that  $[H^+][HSO_3^-] = H_{SO_2}[k_{s1}][p_{SO_2}]$ . In the equilibrium phase, the rate is nearly pH independent for pH>2. But, MARGA is a dynamic absorption system, the SO<sub>2</sub> and S (IV) in the denuder liquid can never be in the equilibrium. All the sampled SO<sub>2</sub> will be absorbed into the denuder liquid, then in the relative higher pH range (higher than 4) both [H<sup>+</sup>] and [HSO<sub>3</sub><sup>-</sup>] will decrease with pH (See Fig. 6a), and thus resulted in a lower oxidation rate.

$$\frac{d[S(IV)]}{dt} = \frac{k[H^+][H_2O_2][HSO_3^-]}{1+K[H^+]} \text{ Eq.3}$$

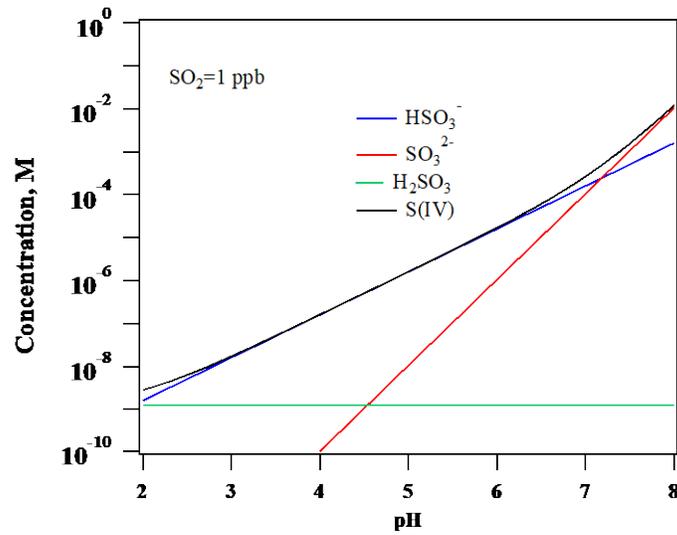


Figure 2 The concentration of S(IV) species as a function of solution pH for 1ppb SO<sub>2</sub>

The oxidation of SO<sub>2</sub> by O<sub>2</sub> is slowly, but can be catalyzed by iron and manganese. But there is almost no aerosol as well as Fe<sup>3+</sup> and Mn<sup>2+</sup> in the denuder solution. Therefore, this reaction was ignored in our study.

Reviwer2

The manuscript compares two methods to measure HONO concentration in the atmosphere. Wet denuder-ion chromatography and long-path absorption photometer are widely used worldwide, but the accuracy of the WD/IC method is still a problem. In this paper, the authors developed a method to correct the HONO concentration measured by MARGA and would be useful to evaluate the WD/IC data. This paper is very interesting and maybe publishable, provided that the following issues are adequately addressed.

Response: we thank the reviewer for the comments and suggestions. We have revised the manuscript accordingly and address the specific comments as follows.

1. The LOPAP has two channels to measure HONO concentration, and the second channel is used to measure the interference, it would be better to add this information in the manuscript and compare this interference with the MARGA result.

Response: Thanks for the suggestion.

We have tried to analyze relationship between second channel of LOPAP and interference with the MARGA at the very beginning of this work. Unfortunately, we cannot get any correlation between the signal of second channel and the measurement interference of Marga. The different sampling method should be the major reason.

2. The reaction of NO<sub>2</sub> on the sample line and aerosol would generate HONO. The correlation between HONO lopap and HONO marga with the influence of PM<sub>2.5</sub>, SO<sub>2</sub>, and NH<sub>3</sub> are discussed. In line 189, the authors conclude that the hydrolysis of NO<sub>2</sub> is not the main source of HONO. So how about the role of relative humidity to this process?

Response: Thanks for the comments, and it's indeed an interesting question.

First, we found weak correlation between the MARGA measurement interference with NO<sub>2</sub> or PM<sub>2.5</sub> (Fig.2 of the manuscript). This suggest that, at least, the NO<sub>2</sub> hydrolysis is not the major contributor to the observed interference.

In term of the NO<sub>2</sub> hydrolysis process, RH will definitely influence the NO<sub>2</sub> hydrolysis in the sampling line, but in a nonlinear way. However, in the ambient air, RH is usually anti-correlated to SO<sub>2</sub>, and resulted in a not bad correlation with the pH and denuder liquid (see the figure below). In such case, RH looks correlated to the measurement interference of

MARGA (Fig. 2a), but the underlying reason is not the  $\text{NO}_2$  hydrolysis.

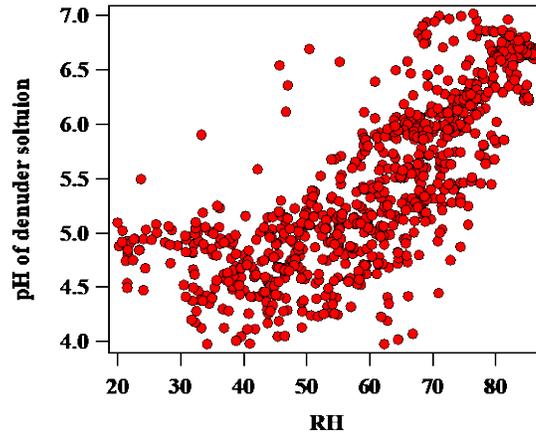


Fig. 1 The correlation between RH and pH of denuder solution

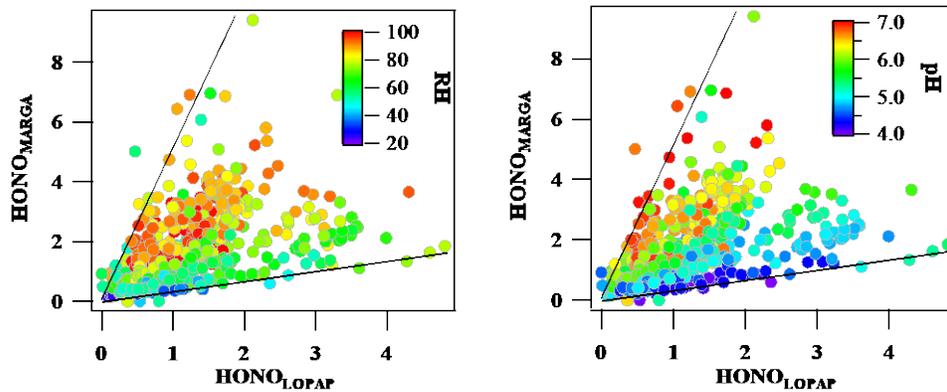


Figure 2. The colored scatter plots between  $\text{HONO}_{\text{marga}}$  and  $\text{HONO}_{\text{lopap}}$  for RH and pH of denuder solution.

But we cannot rule out the influence of  $\text{NO}_2$  hydrolysis. As showed in the following figure, the interference that cannot be explained by the reaction of  $\text{SO}_2$  and  $\text{NO}_2$  showed the some dependence on  $\text{NO}_2$  and RH. The residual (unexplained interference HONO) to  $\text{NO}_2$  ratio have similar dependency on RH as ambient  $\text{HONO}/\text{NO}_2$ . This may indicate the additional role of  $\text{NO}_2$  hydrolysis in inducing measurement interference in the MARGA system. We will have more lab work to dig out the detailed role of  $\text{NO}_2$  hydrolysis on the MARGA measurement interference.

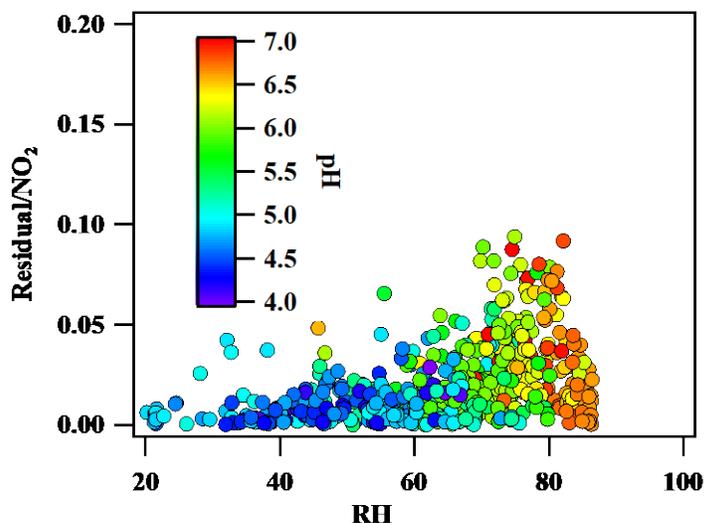


Figure 3. The correlation of residual/ $\text{NO}_2$  with RH. The residual is the difference of  $\text{MARGA}_{\text{int.}}$  and the calculated interference from the reaction of  $\text{SO}_2$  and  $\text{NO}_2$

3. In Fig 6b, the definition of  $\text{PH}_2\text{O}_2^*_{\text{s}}$  and  $\text{PNO}_2^*_{\text{s}}$  should be given in the manuscript. Fig 6a shows the ration between the different fraction of S(IV), in line 310, the ratio of  $\text{HSO}_3^-$  would decrease with the increase of pH, but the concentration would increase slightly.

Response:

We have added the definition of  $\text{P}_{\text{H}_2\text{O}_2^*_{\text{s}}}$  and  $\text{P}_{\text{NO}_2^*_{\text{s}}}$  in the revised manuscript.

The condition in MARGA system is different with ambient air. In the ambient air or an equilibrium state, the concentration of S(IV) species as a function of solution pH for 1ppb  $\text{SO}_2$  just as the figure show, total S(IV) will increase with pH. But, MARGA is a dynamic absorption system, all the sampled  $\text{SO}_2$  will be absorbed into the denuder liquid, the concentration of  $[\text{HSO}_3^-]_{\text{aq}}$  was determined by the fraction of  $\text{HSO}_3^-$  as a function of the pH. In the relative higher pH range (higher than 4),  $[\text{HSO}_3^-]$  will decrease with pH (See Fig. 6a).

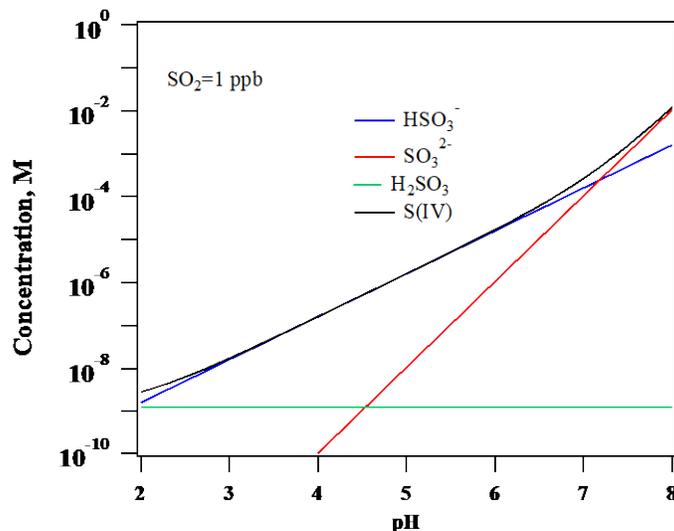
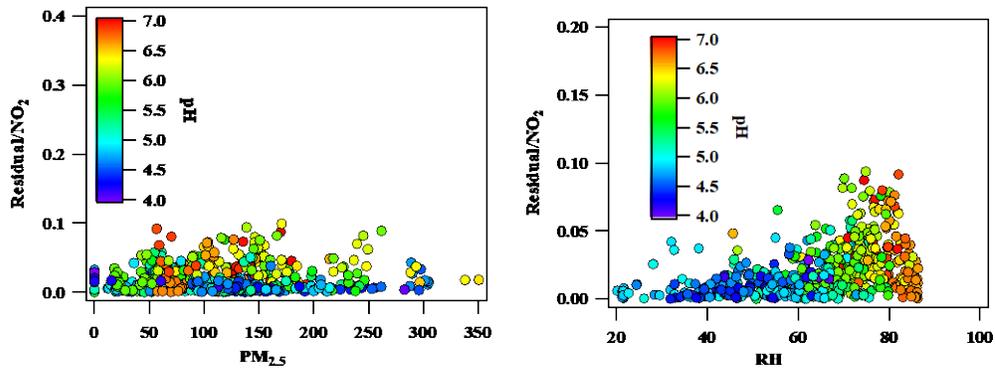


Figure 4 The concentration of S(IV) species as a function of solution pH for 1ppb SO<sub>2</sub>

4. The HONO measured by MARGA was significantly improved after the correction, especially in the clean condition. However, in the polluted condition, the correlation between HONO maga\_corr and HONOlopap become worse, so if it is possible to include the RH and particulate matter parameters in the correction formula?

Response: After correction, there are still interference that cannot be corrected. The dependency of unexplained HONO to NO<sub>2</sub> ratio (residual/NO<sub>2</sub>) on RH is similar with that of ambient HONO/NO<sub>2</sub> on RH which was observed in many other studies, and indicate the NO<sub>2</sub> heterogeneous reaction or the reaction of SO<sub>2</sub> and NO<sub>2</sub> in the sampling tube may be another factors impacting the HONO interference (Su et al., 2008). But in general, these additional interference is not believed to be the major contributor.

As showed in the following figures, the relationship between residual and RH or PM<sub>2.5</sub> are complex, we cannot get a proper equation to reproduce these interference. It will be suffered to large uncertainty in case using a linear regression. However, the main purpose of this paper is to quantify the interference from known reaction by a uniform method in different ambient. According to our current work, we think it is still difficulty to correct the HONO interference using RH and PM<sub>2.5</sub>. Further work is needed.



The correlation of residual/NO<sub>2</sub> with RH. The residual is the difference of MARGA<sub>int.</sub> and the calculated interference from the reaction of SO<sub>2</sub> and NO<sub>2</sub>

Other minor revision:

Response: Thanks for the correction. All the mistakes/typos have been corrected in the revised manuscript.

Line 63 The citation format should be rewritten.

Line 220 “Mg<sup>2+</sup>, Ca<sup>2+</sup>” should change to” Mg<sup>2+</sup>, Ca<sup>2+</sup>”

Line 271 “low PH” should change to “low pH”

Line 345. “NH<sub>3</sub> concentration“ should change to “NH<sub>3</sub> concentration”