Reviwer1

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 r2=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 r2=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 NO2 on the sampling tube or aerosol may introduce the artificial HONO" should be "As the potential source for HONO, the heterogeneous reaction of NO2 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 SO2 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 SO2 concentrations and higher NH3 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_2 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_2 concentration was added into the samples tube together with ambient air with about 13 ppbv NH_3, to adjust the pH of denuder liquid.

"In order to adjust the pH of denuder solution, SO_2 with concentration of 0, 5, 10, 20, 40, 80 and 100 ppbv were injected into the sampling line with the NH_3 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

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

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

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, $HONO_{lopap}/HONO_{marga}$ was about 3. Here, there was a typo in this Fig 4, that the red line should be the reciprocal of collection efficiency $(1/\varepsilon)$ instead of collection efficiency. We have corrected this mistake in the revised manuscript.
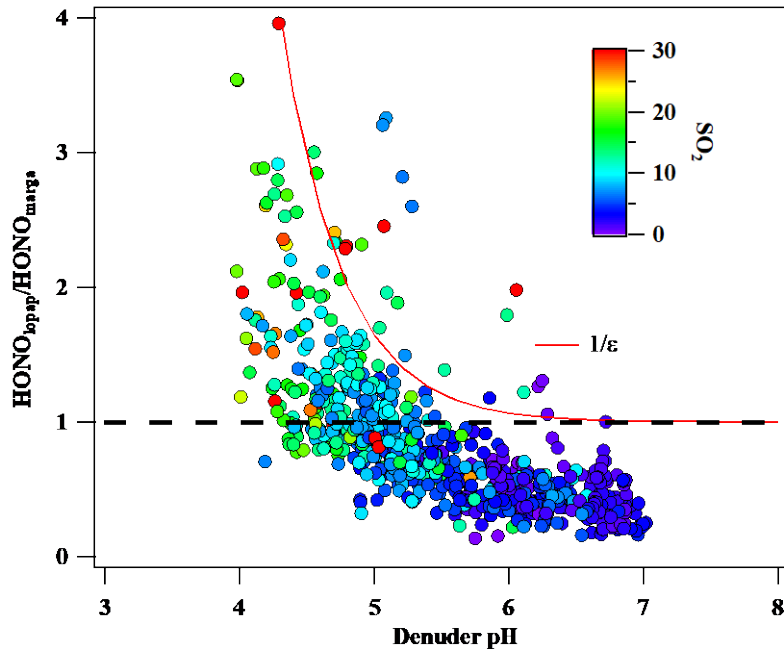
Variation in the ratio of $HONO_{lopap}$ to $HONO_{marga}$ with the denuder absorption solution pH. The red line is the reciprocal of the HONO collection efficiency of MARGA.

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_2 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_2 was hydrolyzed to HONO, suggesting a small contribution of NO_2 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. Lines282-283, 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_2O_2 in MARGA`s denuder solution competitive oxidizing SO_2."

13. Lines 284-285, the competition ("complete SO2 oxidation" in your text may mistyped) oxidation of SO2 by H2O2 and NO2 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_2 oxidation by H_2O_2 and NO_2 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 HSO3-, SO3-, SO2 in liquid should be very fast, the fast oxidation of HSO3- by H2O2 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 H2O2 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 SO2 by O2 also account for large fraction under basic condition, the nearly 100% sulfur oxidation by NO2 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_2 in the ambient air. The oxidation rate of S by H_2O_2 in the liquid phase would follow the equation (Eq. 3). In the ambient air, SO_2 and S(IV) in the aerosol phase are always assumed to be in the equilibrium, that $[H^+][HSO_3^-] = H_{SO2}[k_{s1}][p_{SO2}]$. In the equilibrium phase, the rate is nearly pH independent for pH>2. But, MARGA is a dynamic absorption system, the SO_2 and S (IV) in the denuder liquid can never be in the equilibrium. All the sampled SO_2 will be absorbed into the denuder liquid, then in the relative higher pH range (higher than 4) both $[H^+]$ and $[HSO_3^-]$ will decrease with pH (See Fig. 6a), and thus resulted in a lower oxidation rate.

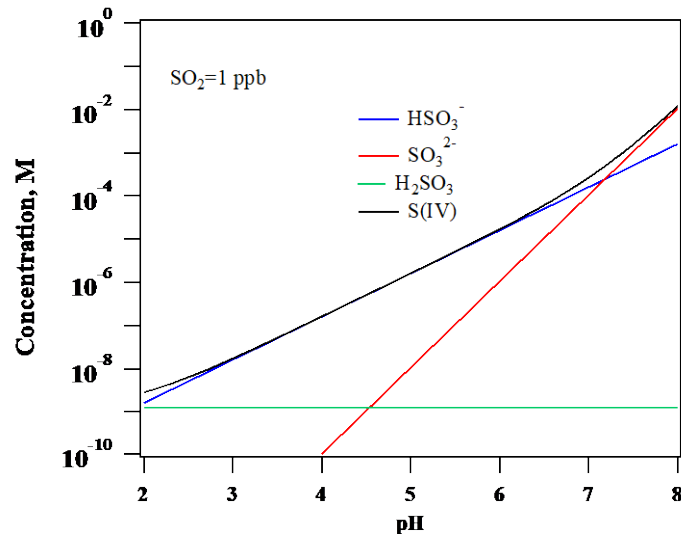$$\frac{d[S(IV)]}{dt} = \frac{k[H^+][H_2O_2][HSO_3^-]}{1+K[H^+]} \quad Eq.3$$

Figure 2 The concentration of S(IV) species as a function of solution pH for 1ppb SO_2

The oxidation of SO_2 by O_2 is slowly, but can be catalyzed by iron and manganese. But there is almost no aerosol as well as Fe^{3+} and Mn^{2+} in the denuder solution. Therefore, this reaction was ignored in our study.