

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 NO₂ on the sample line and aerosol would generate HONO. The correlation between HONO lopap and HONO marga with the influence of PM_{2.5}, SO₂, and NH₃ are discussed. In line 189, the authors conclude that the hydrolysis of NO₂ 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 NO₂ or PM_{2.5} (Fig.2 of the manuscript). This suggest that, at least, the NO₂ hydrolysis is not the major contributor to the observed interference.

In term of the NO₂ hydrolysis process, RH will definitely influence the NO₂ hydrolysis in the sampling line, but in a nonlinear way. However, in the ambient air, RH is usually anti-correlated to SO₂, 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 NO_2 hydrolysis.

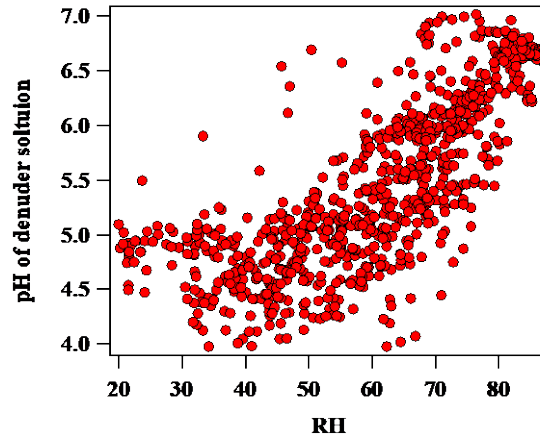


Fig. 1 The correlation between RH and pH of denuder solution

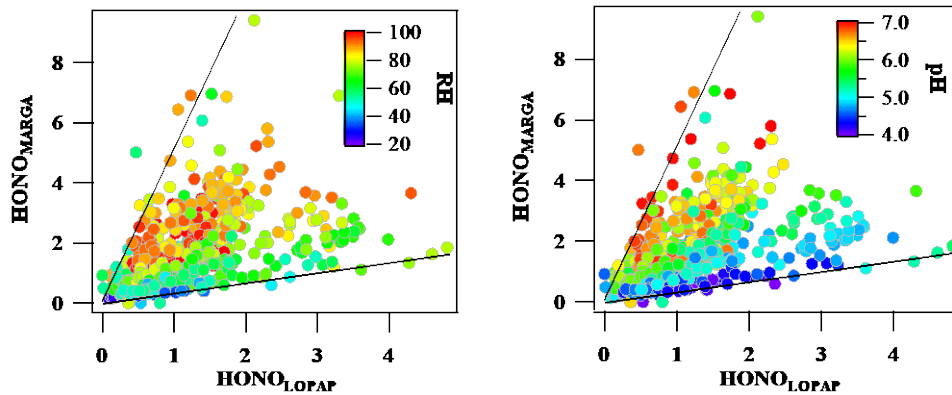


Figure 2. The colored scatter plots between $\text{HONO}_{\text{marga}}$ and $\text{HONO}_{\text{lopap}}$ for RH and pH of denuder solution.

But we cannot rule out the influence of NO_2 hydrolysis. As showed in the following figure, the interference that cannot be explained by the reaction of SO_2 and NO_2 showed the some dependence on NO_2 and RH. The residual (unexplained interference HONO) to NO_2 ratio have similar dependency on RH as ambient HONO/NO_2 . This may indicate the additional role of NO_2 hydrolysis in inducing measurement interference in the MARGA system. We will have more lab work to dig out the detailed role of NO_2 hydrolysis on the MARGA measurement interference.

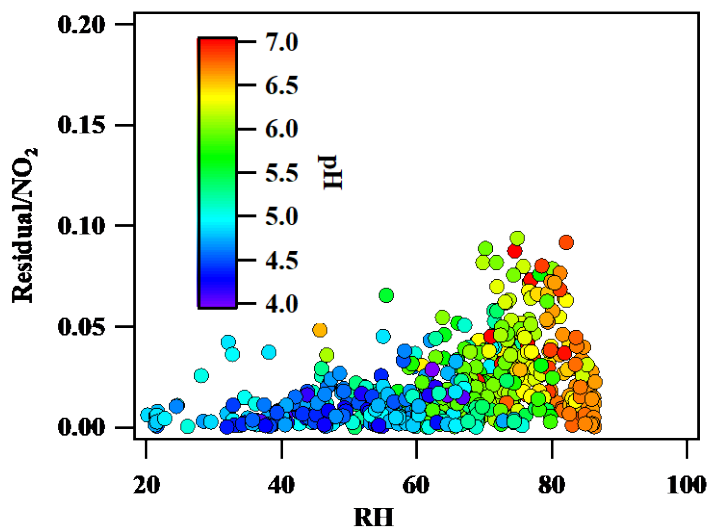


Figure 3. The correlation of residual/ NO_2 with RH. The residual is the difference of $\text{MARGA}_{\text{int.}}$ and the calculated interference from the reaction of SO_2 and NO_2

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 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 SO_2 just as the figure show, total S(IV) will increase with pH. But, MARGA is a dynamic absorption system, all the sampled SO_2 will be absorbed into the denuder liquid, the concentration of $[\text{HSO}_3^-]_{\text{aq}}$ was determined by the fraction of 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).

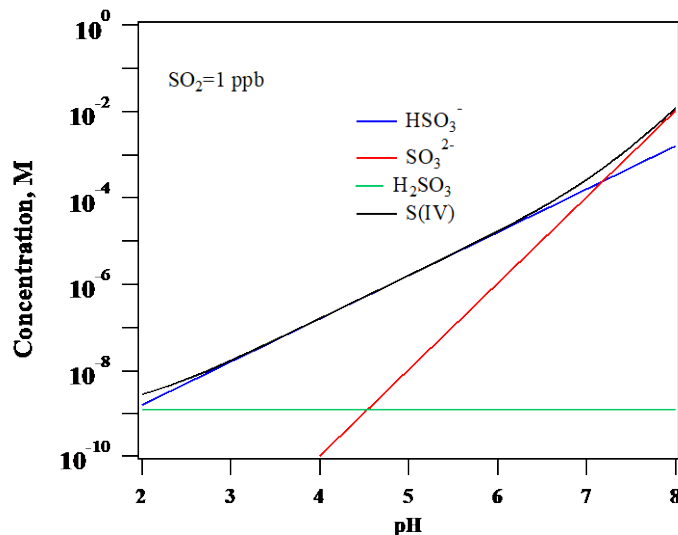
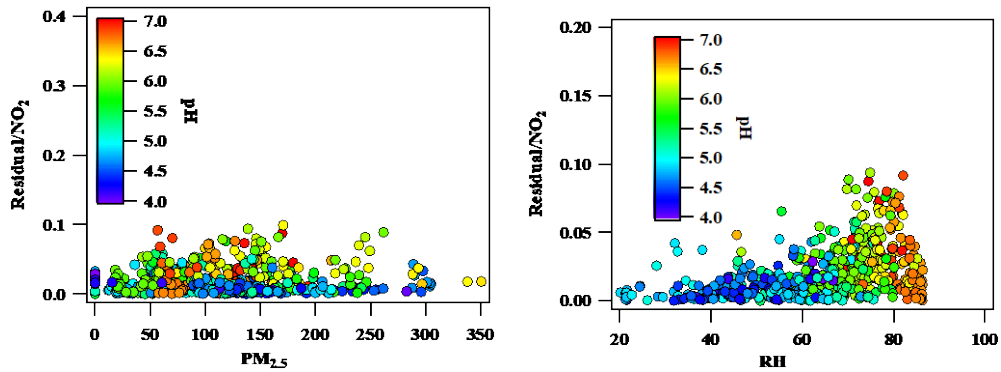


Figure 4 The concentration of S(IV) species as a function of solution pH for 1ppb SO₂

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 NO₂ ratio (residual/NO₂) on RH is similar with that of ambient HONO/NO₂ on RH which was observed in many other studies, and indicate the NO₂ heterogeneous reaction or the reaction of SO₂ and NO₂ 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_{2.5} 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_{2.5}. Further work is needed.



The correlation of residual/NO₂ with RH. The residual is the difference of MARGA_{int.} and the calculated interference from the reaction of SO₂ and NO₂

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 “Mg²⁺, Ca²⁺” should change to” Mg²⁺, Ca²⁺”

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

Line 345. “NH₃ concentration“ should change to “NH₃ concentration”